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## ANOMALOUS APPARENT DIELECTRIC CONSTANTS OF GASES ON SEVERAL POROUS ADSORBENTS<sup>1</sup>

S. E. PETRIE<sup>2</sup> AND R. McINTOSH

### ABSTRACT

Changes in the capacity of a test cell which contained porous Vycor glass have been measured following the adsorption of butane and ethyl chloride. The results are similar to those obtained by Snelgrove and McIntosh using silica gel and these adsorbates. That is, a sudden drop in the apparent polarization is observed at a well defined quantity of adsorbed gas. This observation thus appears characteristic of porous adsorbents. To explain the phenomenon one may postulate a low density for the material of low apparent polarizability, or its location in a different electrical field in the heterogeneous dielectric. The former is ruled out with Vycor glass because of insufficient pore volume. The latter approach has been examined using the "cluster" treatment of Channen and McIntosh with the data for silica gel systems as well as porous glass. The attempt has proved only partially successful.

### INTRODUCTION

In a series of papers from this laboratory, experimental data have been reported showing the effect of an adsorbed gas on the electrical capacity of a cell containing a solid adsorbent (4, 5, 6, 7, 8, 9). These data have been used to calculate apparent dielectric constants of the adsorbed phase. The method of calculation most frequently employed in the papers has been based upon a treatment for solid powders due to Böttcher (6), although other methods have been used for comparison (4). In general, the extended Böttcher treatment has appeared the most satisfactory, because, in the case of the non-polar adsorbate, butane, good agreement with the value for bulk liquid butane at the same temperature has been obtained on non-porous rutile, on activated silica gel, and, as reported below, on porous Vycor glass. In a recent paper the reasons are given why a comparison of computed results with the value of the liquid material is considered valid for a non-polar adsorbate (2). It is concluded that induced dipoles should be of no importance, and unless the electronic and atomic polarizabilities of the adsorbed molecules are seriously modified, the adsorbate should be indistinguishable from bulk matter. Provided, then, that the correct assumption is made regarding the volume fraction of the test cell which is occupied by the adsorbate, the same dielectric constant should be found as for the same substance at the same density in a bulk phase. These statements do not apply to polar adsorbates, because the contribution to polarization made by the orientation of the dipole will presumably differ from that in a bulk phase. It is interesting to note that the variation of the orientational polarization as the surface becomes more nearly saturated makes possible the detection of the completed unimolecular layer on a

<sup>1</sup>Manuscript received November 14, 1956.

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non-porous adsorbent (4, 8, 9). Below the quantity adsorbed required to complete the unimolecular layer, the adsorbed molecules seem to be rotational oscillators. This is suggested by the theoretical predictions (2) that the polarization should be less than for a freely rotating dipole of the same magnitude, and that the temperature dependence of polarization should be negligible to a first approximation. Where experiment, as interpreted with the aid of the extended Böttcher treatment of calculation, indicates that these criteria are met, the adsorbed molecules have been considered to behave as rotational oscillators. Provisionally this seems to be the case for ethyl chloride adsorbed on rutile, in both the first and higher molecular layers, since Channen (3) was unable to detect any temperature coefficient over a 60° range of temperature. It seems surprising, however, that in the higher layers the molecules are not free to rotate.

The most difficult finding to interpret has been the discovery with both polar and non-polar adsorbates on a porous adsorbent, that there is a sudden change of apparent dielectric constant at some critical value of the volume adsorbed (4, 6, 8, 9). (See also Fig. 1.) In the case of butane on silica gel an attempt to explain the finding was made by postulating that the density of the adsorbed film of low apparent dielectric constant was much below the density of the liquid state, which is the value of density normally assumed (6). The required value of density was then calculated, and the value appeared possible since there was sufficient volume in the test cell to accept the matter at that density. In the case of butane on porous glass the pore volume of the glass was known, and it was immediately obvious that such an explanation could not suffice, since the pore volume was too low.

The alternative to this attempt at rationalization was to assume that for some reason the adsorbate, at a critical quantity adsorbed, begins to be taken up in a region where the internal field is quite different from that in which the first quantities adsorbed are located.<sup>3</sup> It should be noted that this effect occurs with porous adsorbents only, and that it is found for both polar and non-polar adsorbates. These facts emphasize that the structure of the adsorbent is what is involved. Moreover, in the case of porous glass, the sudden change of apparent dielectric constant occurs at approximately the amount adsorbed where hysteresis becomes apparent in the adsorption isotherm (See Table I). These data suggest that a correlation exists between the quantity adsorbed at the sudden change of polarization and the quantity required to complete the unimolecular layer. However, this correlation is not found when silica gel is the adsorbent (6). Furthermore, the behavior of polar molecules on non-porous rutile indicates that the completion of the first layer should be marked by an increased polarization. Since also the computation of the quantity in the unimolecular layer requires the use of the B.E.T. equation on a porous adsorbent, it seemed advisable to consider the situation in terms of the experimentally observable quantity adsorbed when appreciable amounts begin to adsorb by what is probably a mechanism of capillary condensation. The inception of the hysteresis loop no doubt marks the beginning of this mechanism, although appreciable adsorption by such means occurs only at greater amounts adsorbed.

The simplest procedure to follow on the assumption of distinct fields was to use the

<sup>3</sup>The expression,  $\delta_2 F_2 = (1/4\pi C_2) \{ \epsilon - \epsilon_1 - [3\epsilon(\epsilon_0 - 1)/(2\epsilon + \epsilon_0)] \delta_2 \} E$ , can readily be developed on the basis of the extended Böttcher treatment. Since the term involving  $\epsilon_0 - 1$  is negligible in the usual range of equilibrium pressures, it follows that  $F_2$  is constant whenever experiment reveals a linear variation of  $\Delta C$  with quantity adsorbed. Where a sudden change of slope occurs in such linear plots, either  $F_2$  or  $C_2$  must be considered to change abruptly. A change of  $C_2$ , the polarizability, of a non-polar adsorbate, seems unlikely, as has been stressed already, so that the variation must be attributed to  $F_2$ . This conclusion is not based upon the assumption of the Onsager cavity field in the voids, since the term involving  $\epsilon_0 - 1$  would be negligible on any reasonable assumption.



extended Böttcher treatment for the first quantities adsorbed since it yields a reasonable value for the dielectric constant of butane. Adsorbate beyond the critical quantity was considered to adsorb within the particle,<sup>4</sup> and a treatment akin to the cluster treatment (4) was applied. Thus, for adsorbed matter greater than the critical quantity, the particle, the void space, and adsorbate within the particle are first treated as a single entity, and its dielectric constant is calculated by means of the extended Böttcher treatment. Next the dielectric constant of the composite is separated, again by the extended Böttcher treatment, into the contributions from the solid and the adsorbed phase.

No very specific remarks may be made about the locations of the adsorbed matter treated in these two ways. The attempted solution of the problem is a purely empirical one to be justified or discarded on the basis of the results obtained. Clearly, from what has been said, the regions have been thought of as external and internal surfaces of the particles, since porous particles are involved. As the data given below will show, the procedure has been only partially successful, and in view of its empirical nature this is not surprising. However, no other suggestion to rationalize the results for non-polar adsorbates on porous adsorbents has been forthcoming, and the attempt which has been made may stimulate discussion and further enquiry.

#### EXPERIMENTAL

The procedures used in obtaining the electrical and adsorption data were essentially those described previously (9). All the electrical measurements in the data given were made at a frequency of 3.70 Mc. per second.

Granules of porous Vycor glass, number 7930, were obtained from Corning Glass Works, Pittsburgh, Pa. The granules were ground when wet in a colloid mill and then dried in an oven at 120° C. The particles, which passed through a 40 mesh screen and were held on a 60 mesh screen, were evacuated in the electrical cell at a temperature of 120° C. until a stick vacuum was obtained at 120° C.

The pore volume of the glass, 37.0%, was calculated from the quantity of water the glass would adsorb at a relative pressure close to saturation, as determined from data obtained by Amberg (1), and with the assumption that the density of the adsorbed phase was that of the bulk liquid at the same temperature. In the calculations reported below, a value of 0.45 cc. per gram was taken as the pore volume of the silica gel. This value was supplied by the Davison Chemical Corp., Baltimore, Maryland.

#### RESULTS

##### *The Non-polar Adsorbate, Butane*

Plots of the change of capacitance of the test cell filled with glass versus volume of butane adsorbed at various temperatures are illustrated in Fig. 1 (note the resemblance to the plots of butane on silica gel illustrated in Fig. 5 of Ref. 7). The plots show two linear sections of which the second has a lower slope than the first. Extrapolation of the lines defines a critical value of the quantity of gas adsorbed on the Vycor glass at which a sudden change in the apparent polarization of the adsorbed phase occurs. Over the temperature range studied, the temperature coefficient is negligible. Within experimental error, the position of the discontinuity of the slope is independent of temperature, and it

<sup>4</sup>Professor J. J. Hermans in a private communication has suggested the use of a porous block of the adsorbent. This would eliminate voids between particles and restrict the type of void to the range of sizes in the porous adsorbent.

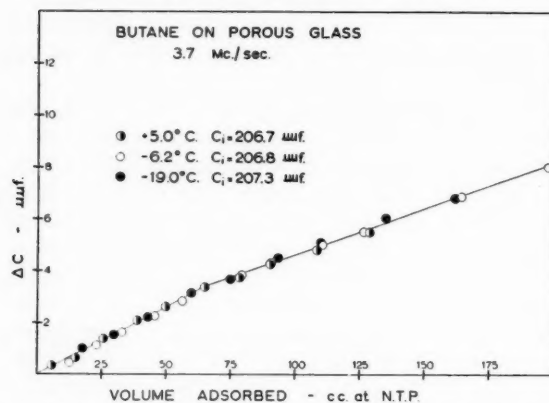


FIG. 1. Plots of capacity increments versus quantity adsorbed for butane on porous Vycor glass.

occurs at a quantity of gas adsorbed somewhat below the beginning of the hysteresis loop. Typical values of the volumes of gas adsorbed at the inception of the hysteresis loop, the position of the discontinuity of the slope, and the completion of the unimolecular layer are given in Table I, for both butane and ethyl chloride adsorbed on Vycor glass.

TABLE I  
A COMPARISON OF SIGNIFICANT QUANTITIES ADSORBED (CC. AT N.T.P.)

Adsorbate	Temp., °C.	Vol. adsorbed at inception of hysteresis loop	Vol. adsorbed at position of discontinuity	Vol. adsorbed at completion of monolayer
Butane	-6.4	95	68	78
Ethyl chloride	14.4	120	95	99

In Table II, the dielectric constants calculated by means of the extension of Böttcher's powder method are given for butane adsorbed on porous glass. The density of the adsorbed phase was assumed to be that of the bulk liquid at the same temperature.

Although there appears to be good agreement between the values of the dielectric constant for the first linear section and those of the bulk liquid, the values along the

TABLE II  
DIELECTRIC DATA FOR BUTANE ON POROUS VYCOR GLASS  
(Capacitance of empty cell, 111.0  $\mu\text{mf.}$  Weight of adsorbent, 7.23 g. Density of adsorbent, 2.29 g./cc.)

Temp., °C.	Dielectric constant from the extended Böttcher treatment		Dielectric constant from the cluster treatment		Refractive index squared
	First linear section	Second linear section	First linear section	Second linear section	
5.0	1.89	1.60	1.81	1.61	1.81
-6.2	1.85	1.52	1.80	1.63	1.83
-19.0	1.88	1.55	1.82	1.64	1.84

second linear section are somewhat lower. Similar data have been reported by Snelgrove, Greenspan, and McIntosh (7) for butane adsorbed on dry silica gel.

In the work of Snelgrove, Greenspan, and McIntosh, different types of adsorption sites were postulated as a possible explanation for the sudden change in the dielectric properties. By varying the condition of the adsorbing surface with the addition of various known quantities of water prior to adsorption of butane it was hoped that information concerning the adsorption sites could be obtained. The critical quantity of butane adsorbed decreased as the quantity of water increased, until several hundred cc. of water measured at N.T.P. had been adsorbed, and then, it remained constant. The polarizations of both linear sections decreased as the quantity of water increased. The decrease for the second section, however, was greater than for the first. This caused an increasing separation between the values of the dielectric constants for the two regions. The dielectric results are tabulated in Table III.

TABLE III

DIELECTRIC DATA FOR BUTANE ON SILICA GEL  
(Capacitance of empty cell, 113.5  $\mu\text{f}$ . Weight of adsorbent, 6.20 g. Density of adsorbent, 2.20 g./cc.)

Temp., °C.	Water content, cc. at N.T.P.	Dielectric constant from the extended Böttcher treatment		Dielectric constant from the cluster treatment		Refractive index squared
		First linear section	Second linear section	First linear section	Second linear section	
0.1	Nil	1.79	1.63	1.74	1.70	1.81
0.1	44.6	1.74	1.61	1.68	1.70	1.81
0.1	89.1	1.74	1.58	1.72	1.63	1.81
0.1	167.3	1.70	1.55	1.69	1.66	1.81
0.1	360.8	1.70	1.49	1.67	1.63	1.81

The extension to Böttcher's powder method gives dielectric constants along the first linear sections that agree fairly well with those of the bulk liquid for a non-polar adsorbate. It fails to give, however, a common value of the dielectric constant for the two regions. Since the concept of a low density proved to be erroneous, the abrupt change in the apparent polarization must be caused by a change in the field. The apparent polarization remains constant throughout the hysteresis loop, and it is independent of whether measurements are obtained on adsorption or desorption in this region. It was assumed, therefore, that the field in the pores was different from that in the voids between particles. Along the first region, it was postulated that adsorption took place on the surfaces between particles, and that the extension to Böttcher's powder method was applicable. The adsorbent volume fraction included the pore volume fraction. After the critical volume was reached, adsorption was regarded as taking place within the pores. If the particle, its pore volume, and the gas adsorbed in the pores are treated as an entity in the second region, an application of the extended Böttcher formula yields an average dielectric constant for the particles, when the polarization and the volume fraction of the adsorbed phase in the initial adsorption region are regarded as constant to a first approximation. The average dielectric constant obtained in this manner can be separated by means of the extended Böttcher treatment into contributions from the solid and the adsorbed phase. The void

volume fraction is now the pore volume fraction that is not occupied by the adsorbed film.

An assumption had to be made regarding the distribution of the water between the two adsorption regions of the silica gel prior to the adsorption of butane. When the water alone is adsorbed on the silica gel, the sudden change of apparent polarization does not occur until 235 cc. (of gas at N.T.P.) is adsorbed. It was assumed, therefore, that quantities of water below this amount would be adsorbed in the first adsorption region, and that the quantities in excess of this amount would be adsorbed in the second. The free space between granules and within granules was computed from these assumptions, and modified, of course, because of the butane which was subsequently added.

The dielectric data calculated from the cluster method are given in Tables II and III for Vycor glass and silica gel respectively.

#### *The Polar Adsorbates, Ethyl Chloride and Water*

Plots of the change of capacitance of the test cell containing Vycor glass versus volume adsorbed for a polar adsorbate resemble those for a non-polar adsorbate (Fig. 2). Similar

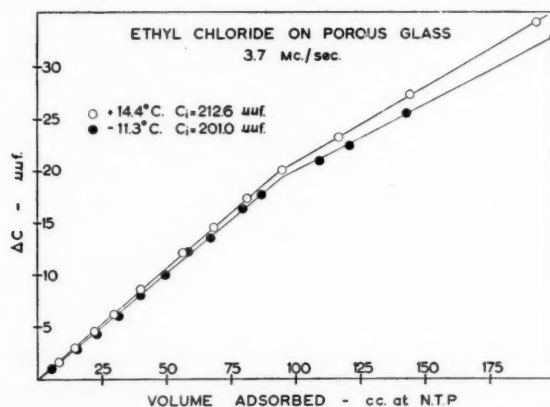


FIG. 2. Plots of capacity increments versus quantity adsorbed for ethyl chloride on porous Vycor glass.

plots were obtained with water and ethyl chloride on silica gel (7). Again, the critical quantity of gas adsorbed is independent of temperature. With ethyl chloride adsorbed on silica gel, the critical quantity of adsorbed gas decreases as the amount of water adsorbed prior to adsorption of ethyl chloride increases.

The dielectric results calculated from the extension to Böttcher's powder method and the cluster method are given in Tables IV, V, and VI. In applying the cluster treatment, void space between and within particles was calculated as it was for butane. The results for water are considerably improved, but those for ethyl chloride only slightly. Over the temperature range studied the temperature coefficient of the polarization of ethyl chloride is small, and that for water is zero within experimental error along the first linear section. These results are somewhat similar to those obtained by Channen for ethyl chloride on rutile (3).

TABLE IV

DIELECTRIC DATA FOR ETHYL CHLORIDE ON POROUS VYCOR GLASS  
(Capacitance of empty cell, 113.0  $\mu\text{f}$ . Weight of adsorbent, 7.05 g. Density of adsorbent, 2.29 g./cc.)

Temp., °C.	Dielectric constant from the extended Böttcher treatment		Dielectric constant from the cluster treatment		Dielectric constant from Onsager equation
	First linear section	Second linear section	First linear section	Second linear section	
14.4	8.65	4.53	6.41	4.68	10.5
-11.3	7.68	4.45	6.57	4.60	11.8

TABLE V

DIELECTRIC DATA FOR ETHYL CHLORIDE ON SILICA GEL  
(Capacitance of empty cell, 113.5  $\mu\text{f}$ . Weight of adsorbent, 6.20 g. Density of adsorbent, 2.20 g./cc.)

Temp., °C.	Water content, cc. at N.T.P.	Dielectric constant from the extended Böttcher treatment		Dielectric constant from the cluster treatment		Dielectric constant from Onsager equation
		First linear section	Second linear section	First linear section	Second linear section	
30.0	Nil	5.85	4.00	4.90	4.06	9.75
0.0	Nil	6.59	4.08	5.39	4.54	11.2
-30.0	Nil	7.20	4.20	6.01	4.93	12.9
0.1	85.3	5.94	4.08	5.23	4.27	11.2
0.1	175.2	5.66	4.04	5.14	4.20	11.2
0.1	249.7	5.25	4.06	4.88	4.18	11.2

TABLE VI

DIELECTRIC DATA FOR WATER ON SILICA GEL  
(Capacitance of empty cell, 115.7  $\mu\text{f}$ . Weight of adsorbent, 6.23 g. Density of adsorbent, 2.20 g./cc.)

Temp., °C.	Dielectric constant from the extended Böttcher treatment		Dielectric constant from the cluster treatment		Dielectric constant from International Critical Tables
	First linear section*	Second linear section	First linear section	Second linear section	
44.0	—	49.7	69.2	45.0	70.4
30.0	—	69.1	69.2	61.0	76.4
9.0	—	44.9	61.0	47.2	84.4
-6.0	—	54.6	74.2	41.5	90.4†
-15.0	—	64.7	69.2	40.0	94.6†

\*Polarization is greater than one.

†Estimated dielectric constant for subcooled water.

## DISCUSSION

It can be seen that the attempt to deal separately with the two linear sections of the data, characteristic of all gases on porous adsorbents, is only partially successful. The effect of the method of computation is, in general, to lower the value of the dielectric constant along the first region to some extent, and to raise that of the second region



slightly. In two cases only are the changes sufficient to suggest that the procedure has merit. For butane on both dry and wet silica gel the values are seen to be quite similar for both adsorption regions, although they are now somewhat lower than the refractive index value. For water on silica gel the anomalous value of polarization (greater than 1.0) for the first region is reduced and a value quite close to that for liquid water is obtained. However, the disparity between values for the two adsorption regions still persists for this latter case. The inequality also remains for ethyl chloride on silica gel, whether wet or dry. Similarly, there is insufficient change to bring the values for both linear sections into agreement for any adsorbate on Vycor glass.

In view of these findings, it is clear that employment of the cluster treatment for the adsorbed matter along the second linear section is not an adequate solution to the problem. Since, however, an assignment of a low density value to the adsorbate for this region has been proved incorrect, some type of treatment which accounts for a difference in fields must be sought. That the experimental observation of an apparently low polarization seems specific to porous adsorbents is surely significant. It then appears mandatory to attribute the effect to the existence of pores and a different electrical field within them. As the inception of hysteresis in the isotherm and the sudden change of apparent polarization occur at approximately the same quantity adsorbed, a belief in the essential correctness of this type of attack on the problem is strengthened.

#### ACKNOWLEDGMENT

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We are indebted to E. W. Channen for valuable discussions.

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# THE INFRARED AND RAMAN SPECTRA OF DISULPHUR DECAFLUORIDE (S<sub>2</sub>F<sub>10</sub>)<sup>1</sup>

J. K. WILMSHURST<sup>2</sup> AND H. J. BERNSTEIN

## ABSTRACT

The infrared spectrum of S<sub>2</sub>F<sub>10</sub> has been obtained for the vapor from 5 to 35  $\mu$  and for the solid at liquid nitrogen temperatures from 10 to 24  $\mu$ . The Raman spectrum, together with depolarization ratios, was obtained for the liquid. A vibrational assignment has been made consistent with either  $D_{4d}$  or  $D_{4h}$  symmetry and all the fundamentals identified except two low FSSF bending frequencies and the inactive torsional frequency. A normal co-ordinate calculation located the bending frequencies at 37 and 57 cm.<sup>-1</sup> while a simple potential energy calculation gave a torsional frequency of 89 cm.<sup>-1</sup> corresponding to a potential barrier of 2780 cm.<sup>-1</sup>.

The infrared spectrum only of disulphur decafluoride has previously been reported from 7 to 20  $\mu$  (3, 4). From electron diffraction measurements (6) the molecule has been shown to be a symmetric top consisting of two octahedral SF<sub>6</sub> groups linked together with an S—S bond in a dumbbell type structure. The relative orientation of the two SF<sub>6</sub> groups with respect to each other, corresponding to an eclipsed or staggered model (point symmetry  $D_{4h}$  or  $D_{4d}$  respectively), was not determined. For this particular molecule, the selection rules for the vapor, concerning the fundamental and binary overtone and combination frequencies, give the same allowed Raman and infrared transitions, depolarization ratios, and band envelopes for both point groups  $D_{4d}$  and  $D_{4h}$ .

In the present investigation the Raman spectrum of the liquid with depolarization ratios was obtained, and the infrared spectrum of the vapor was extended to cover the 5–35  $\mu$  region. The infrared spectrum of the solid at liquid nitrogen temperatures was also obtained from 10 to 24  $\mu$ . With the aid of some normal co-ordinate calculations all the fundamentals could be assigned to observed bands on the basis of  $D_{4h}$  or  $D_{4d}$  symmetry, with the exception of the two low lying skeletal bending frequencies and the inactive torsional mode. The low bending frequencies were calculated to be 57 cm.<sup>-1</sup> and 37 cm.<sup>-1</sup> from the normal co-ordinate calculation (Appendix 1), while the torsional frequency was calculated, assuming  $D_{4d}$  symmetry, to lie at 89 cm.<sup>-1</sup> (Appendix 2).

The infrared spectrum of solid S<sub>2</sub>F<sub>10</sub> and its assignment indicated that the crystal site symmetry has, at most, a twofold axis.

## EXPERIMENTAL

The sample of S<sub>2</sub>F<sub>10</sub> (purified as in Ref. 6) was kindly made available by Dr. J. Dale of the Defence Research Laboratories, Ottawa. The Raman spectrum of the liquid\* was obtained with a White grating Raman spectrometer with photoelectric recording (10), the depolarization ratios being determined by the method of Edsall and Wilson (5)

<sup>1</sup>Manuscript received November 13, 1956.

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<sup>2</sup>National Research Laboratories Postdoctorate Research Fellow 1955–.

\*The Raman spectrum was obtained and measured by Dr. G. Allen while a National Research Laboratories Postdoctorate Research Fellow, 1954.

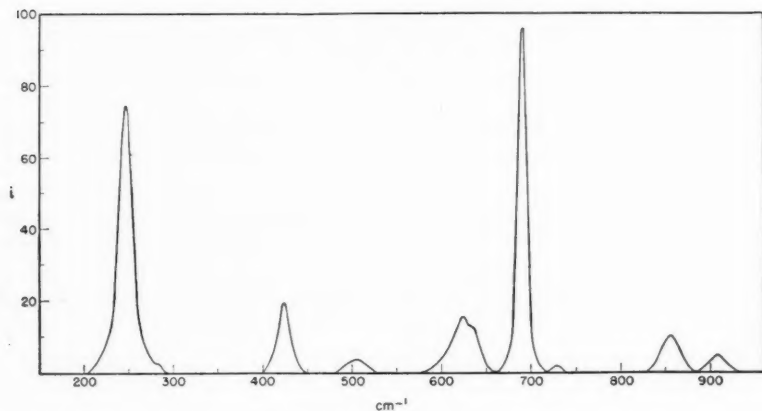


FIG. 1. The Raman spectrum of  $S_2F_{10}$  in the liquid state. Slit width  $\sim 6 \text{ cm}^{-1}$ .

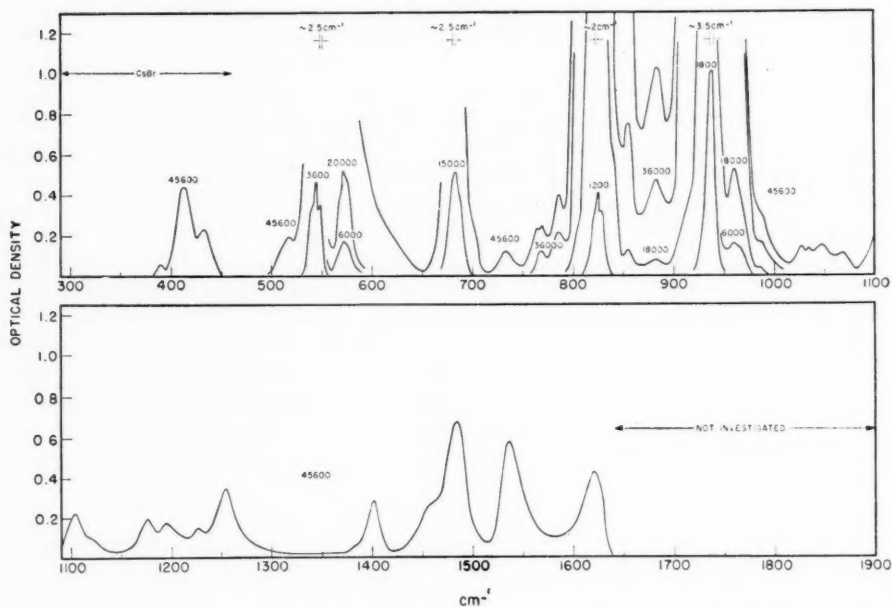
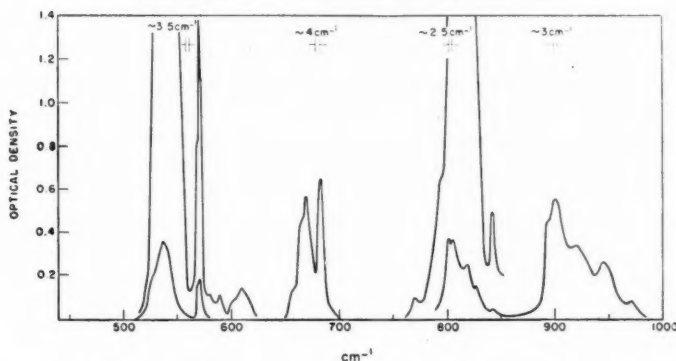


FIG. 2. The infrared spectrum of  $S_2F_{10}$  in the vapor state. The numbers on the chart are the product of cell length in mm. times vapor pressure in mm.

and corrected for convergence error (8). The infrared spectra were obtained with a Perkin Elmer model 12C double pass spectrometer equipped with NaCl, KBr, and CsBr prisms, the spectrum of the vapor being obtained from 5 to  $35 \mu$  and that of the solid at liquid nitrogen temperatures from 10 to  $24 \mu$ .

FIG. 3. The infrared spectrum of S<sub>2</sub>F<sub>10</sub> in the solid state at liquid nitrogen temperature.TABLE I  
VIBRATIONAL SELECTION RULES

Designation	Approximate description	$D_{4h}$		$D_{4d}$	
		Species	Activity	Species	Activity
$\nu_1$	S-F stretching	$A_{1g}$	R. pol.	$A_1$	R. pol.
$\nu_2$	S-F' stretching	$A_{1g}$	R. pol.	$A_1$	R. pol.
$\nu_3$	FSF' bending	$A_{1g}$	R. pol.	$A_1$	R. pol.
$\nu_4$	S-S stretching	$A_{1g}$	R. pol.	$A_1$	R. pol.
$\nu_5$	Torsion	$A_{1u}$	Inactive	$B_1$	Inactive
$\nu_6$	S-F stretching	$A_{2u}$	I.	$B_2$	I.
$\nu_7$	S-F' stretching	$A_{2u}$	I.	$B_2$	I.
$\nu_8$	FSF' bending	$A_{2u}$	I.	$B_2$	I.
$\nu_9$	S-F' stretching	$B_{1g}$	R. depol.	$E_2$	R. depol.
$\nu_{10}$	S-F' stretching	$B_{2u}$	Inactive		
$\nu_{10}'$	F'SF' bending	$B_{2g}$	R. depol.	$E_2$	R. depol.
$\nu_{10}''$	F'SF' bending	$B_{1u}$	Inactive		
$\nu_{11}$	FSF' bending	$B_{1g}$	R. depol.	$E_2$	R. depol.
$\nu_{11}'$	FSF' bending	$B_{1u}$	Inactive		
$\nu_{12}$	S-F' stretching	$E_g$	R. depol.	$E_3$	R. depol.
$\nu_{13}$	FSF' bending	$E_g$	R. depol.	$E_3$	R. depol.
$\nu_{14}$	FSF' bending	$E_g$	R. depol.	$E_3$	R. depol.
$\nu_{15}$	FSS bending	$E_g$	R. depol.	$E_3$	R. depol.
$\nu_{16}$	S-F' stretching	$E_u$	I. $\perp$	$E_1$	I. $\perp$
$\nu_{17}$	FSF' bending	$E_u$	I. $\perp$	$E_1$	I. $\perp$
$\nu_{18}$	FSF' bending	$E_u$	I. $\perp$	$E_1$	I. $\perp$
$\nu_{19}$	FSS bending	$E_u$	I. $\perp$	$E_1$	I. $\perp$

F' refers to a fluorine atom not on the figure axis.

F refers to a fluorine atom on the figure axis.

R., I., pol., and depol. are for Raman, infrared, polarized, and depolarized respectively.

|| = parallel type band, weak Q branch, PR spacing  $\sim 8$  cm.<sup>-1</sup> $\perp$  = perpendicular type band, pronounced Q branch (using bond lengths ( $\theta$ )  $r_{SS} = 1.56$ ,  $r_{SF} = 2.20$ ,  $\angle FSF = 90^\circ$ ).

Figs. 1, 2, and 3 show the Raman spectrum of the liquid and the infrared spectrum of the vapor and solid respectively. Table I gives the selection rules for the two possible molecular symmetries  $D_{4h}$  and  $D_{4d}$ , Table II the observed Raman and infrared bands for the liquid and vapor respectively and their assignments, and Table IV the observed infrared bands for the solid and their assignments.

TABLE II  
 VIBRATIONAL ASSIGNMENT FOR  $S_2F_{10}$ 

Infrared, $\text{cm}^{-1}$ (vapor)	Raman, $\text{cm}^{-1}$ (liquid)	Depol. ratio (corrected)	Assignment ( $D_{4d}$ symmetry)
(37) <sup>a</sup>	(57) <sup>a</sup>		$\nu_{10}(e_1)$
	(89) <sup>a</sup>		$\nu_{15}(e_2)$
	246	0.43	$\nu_5(b_1)$
	283		$\nu_4(a_1)$
390			$\nu_{11}(e_2)$
412	423	0.74	$\nu_3 - \nu_{19} = 386(E_1)$
432	504	0.77	$\nu_8(b_2)$
517			$\nu_9(a_1) = 437(B_2)$
~540			$\nu_{10}(e_2)$
544			$\nu_8 - \nu_3 = 515(B_2)$
548			$\nu_{18}(e_1)$
~567			
571			$\nu_{17}(e_1)$
576			
	624	0.86	$\nu_{14}(e_2)$
	634	0.70	$\nu_{13}(e_2)$
683	690	0.16	$\nu_7(b_2)$
~701 sh <sup>b</sup>	728	?	$\nu_2(a_1)$
733			$\nu_6 - \nu_4 = 692(B_2)$
764			$\nu_9(e_2)$
770			$\nu_7 + \nu_{15} = 740(E_1)$
786			$\nu_{12} - \nu_5 = 767(E_1)$
~820			$\nu_{16} - \nu_{15} = 769(B_1 + B_2 + E_2)$
826			$\nu_4 + \nu_{18} = 790(E_1)$
828			
~841 sh			$\nu_{16}(e_1)$
855			$\nu_3 + \nu_8 = 835(B_2)$
883	856	0.86	$\nu_{11} + \nu_{17} = 854(E_1 + E_2)$
~915 sh	908	0.27	$\nu_{12}(e_2)$
938			$\nu_{15} + \nu_{16} = 883(B_1 + B_2 + E_2)$
~942 sh			$\nu_1(a_1)$
960			$\nu_4 + \nu_7 = 929(B_2)$
~966 sh			$\nu_6(b_2)$
987			$\nu_5 + \nu_{12} = 945(E_1)$
1027			$\nu_3 + \nu_{17} = 994(E_1)$
1035			$\nu_8 + \nu_{14} = 1036(E_1)$
1047			$\nu_5 + \nu_{13} = 1046(E_1)$
1068			$\nu_{10} + \nu_{18} = 1048(E_1 + E_2)$
1104			$\nu_4 + \nu_{16} = 1072(E_1)$
~1122 sh			$\nu_3 + \nu_7 = 1106(B_2)$
1176			$\nu_{10} + \nu_{14} = 1128(E_1 + E_2)$
1195			$\nu_6 + \nu_4 = 1184(B_2)$
1227			$\nu_{14} + \nu_{17} = 1195(B_1 + B_2 + E_2)$
1254			$\nu_2 + \nu_{18} = 1234(E_1)$
1401			$\nu_2 + \nu_{17} = 1261(E_1)$
~1458 sh			$\nu_{12} + \nu_{18} = 1400(B_1 + B_2 + E_2)$
1484			$\nu_{13} + \nu_{16} = 1460(B_1 + B_2 + E_2)$
1536			$\nu_1 + \nu_{17} = 1478(E_1)$
1620			$\nu_7 + \nu_{12} = 1539(E_1)$
			$\nu_2 + \nu_6 = 1628(B_2)$

<sup>a</sup>Calculated.<sup>b</sup>sh = shoulder.



## DISCUSSION

The previously reported infrared spectra of S<sub>2</sub>F<sub>10</sub> (3, 4) are contained in the more complete spectrum obtained in the present investigation with the exception of a few minor bands that were reported as weak in the previous data. The Raman spectrum was complicated to a small extent by an enhancement of the grating ghosts due to slight photodecomposition of the S<sub>2</sub>F<sub>10</sub>, which had been exposed to the Hg arc without NaNO<sub>2</sub> filter. This did not unduly affect the analysis of the spectrum.

The vibrational assignment for this molecule is best discussed under the respective symmetry species. Throughout the discussion the species will be written assuming the molecule has *D*<sub>4d</sub> symmetry with the corresponding species in brackets for *D*<sub>4h</sub> symmetry.

*The a<sub>1</sub>(a<sub>1g</sub>) Vibrations*

Normally, the totally symmetric vibrational frequencies of a molecule are strongly polarized and can be assigned immediately on the basis of the Raman polarization data. With S<sub>2</sub>F<sub>10</sub>, however, though the selection rules show that there should be four totally symmetric frequencies, only three bands at 908, 690, and 246 cm.<sup>-1</sup> are observed to be strongly polarized and these can be assigned with reasonable certainty to  $\nu_1$ ,  $\nu_2$ , and  $\nu_4$ , respectively. The remaining totally symmetric frequency  $\nu_3$  arises from an FSF' bending vibration, which, from the geometry, can be seen to be nearly a pure bending mode and is therefore expected to be only weakly polarized (7).

The bands most likely to arise from this FSF' bending vibration are those at 504 cm.<sup>-1</sup>, 423 cm.<sup>-1</sup>, or perhaps a band nearly coincident with that at 246 cm.<sup>-1</sup>. To distinguish between these possibilities a simple normal co-ordinate calculation was performed using a potential energy function of the form

$$2V_{a_1} = k_1 Q_{SS}^2 + 2k_2 Q_{SF}^2 + 8k_3 Q_{SF'}^2 + (8k_6 + 8k_7) \delta_{FSF'}^2 + (8e_1 - 8e_2) Q_{SS} \delta_{FSF'}$$

for the *a*<sub>1</sub> modes, where the force constants are defined in the more general force field in Appendix 1. There are four force constants (or linear combinations of force constants) and it is possible to calculate all four by using the three observed frequencies  $\nu_1$ ,  $\nu_2$ , and  $\nu_4$  and any one of the possibilities for  $\nu_3$ . This was performed for  $\nu_3 = 504$ , 423, and 246 cm.<sup>-1</sup> in turn and the results (Table III) indicate that the assignment  $\nu_3 = 423$  cm.<sup>-1</sup>

TABLE III  
FORCE CONSTANTS CALCULATED FROM THE *a*<sub>1</sub> FREQUENCIES

Assignment for $\nu_3$	$k_1$	$k_2$	$k_6 + k_7$	$e_1 - e_2$
504	3.84	5.33	3.18	-1.16
423	2.95	5.33	1.75	-0.63
246	0.84	5.33	0.33	Imaginary

gives a value for  $k_1$ , the SS stretching force constant, in line with the values 2.5 in H<sub>2</sub>S<sub>2</sub>(11) and 2.04 in S<sub>8</sub> (2).

*The b<sub>2</sub>(a<sub>2u</sub>) Vibrations*

The *b*<sub>2</sub> vibrational frequencies would be expected to be very similar to the *a*<sub>1</sub> type frequencies, since the only difference in the vibrational modes is that in the *a*<sub>1</sub> modes

both  $SF_6$  groups are vibrating in phase, while in the  $b_2$  modes the  $SF_6$  groups are vibrating out of phase. Thus the observed bands at 938, 683, and  $412\text{ cm}^{-1}$  are assigned to  $\nu_6$ ,  $\nu_7$ , and  $\nu_8$  respectively by analogy with  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$ .

#### *The $e_2(b_{1g}, b_{2g}, b_{1u}, b_{2u})$ Vibrations*

$\nu_9$ , the  $SF'$  stretching mode, would be expected to occur around  $690\text{ cm}^{-1}$  analogous to  $\nu_2$  and  $\nu_7$ , and is associated with the observed Raman band at  $728\text{ cm}^{-1}$ . From a normal co-ordinate calculation (see Appendix 1) using the bending force constant determined from  $SF_6$  (12), the  $F'SF'$  bending frequency  $\nu_{10}$  was calculated to be  $524\text{ cm}^{-1}$ , identifying the observed Raman band at  $504\text{ cm}^{-1}$  with this mode. The remaining  $F'SF$  bending frequency  $\nu_{11}$  was not obvious from the Raman spectrum but a normal co-ordinate calculation using the bending force constants obtained from the more general treatment of the  $a_1$  and  $b_1$  frequencies (Appendix 1) gave a calculated frequency at  $275\text{ cm}^{-1}$ . In the observed Raman spectrum a weak band does occur at  $283\text{ cm}^{-1}$  but this is at the exact frequency of one of the grating ghosts in the Raman spectrometer which may possibly obscure  $\nu_{11}$ . However, assuming the relative intensities of the ghost bands to remain constant from spectrum to spectrum, this band is estimated to have about twice the intensity of the usual ghost at  $283\text{ cm}^{-1}$ . Thus  $\nu_{11}$  could be assigned to the band at  $283\text{ cm}^{-1}$ . Of course,  $\nu_{11}$ , which should be expected to occur only weakly, may actually be hidden under the strong band at  $246\text{ cm}^{-1}$ . The former assignment, however, is chosen in the present discussion.

#### *The $e_1(e_u)$ Vibrations*

The  $e_1$  vibrations should give rise to perpendicular type bands with a pronounced  $Q$  branch. Three such bands were observed at 826, 571, and  $544\text{ cm}^{-1}$  and these are assigned to  $\nu_{16}$ ,  $\nu_{17}$ , and  $\nu_{18}$  respectively. The remaining type  $e_1$  mode,  $\nu_{19}$ , corresponding to a bending of the linear  $FSSF$  chain would be expected to occur at a low frequency and was not observed. However, from a normal co-ordinate calculation (Appendix 1)  $\nu_{19}$  was calculated to be  $37\text{ cm}^{-1}$ .

#### *The $e_3(e_g)$ Vibrations*

The  $e_1$  and  $e_3$  vibrations differ only in that in the former the two  $SF_6$  groups are vibrating in phase, while in the latter they are vibrating out of phase. Thus the  $e_1$  and  $e_3$  frequencies should be very similar, with the  $e_3$  frequencies being slightly greater than the  $e_1$  modes because of the difference in coupling between the two  $SF_6$  groups in the different vibrational species. With this in mind, therefore, the three remaining observed Raman bands at 856, 634, and  $624\text{ cm}^{-1}$  are assigned to  $\nu_{12}$ ,  $\nu_{13}$ , and  $\nu_{14}$  respectively.

As with the  $e_1$  modes,  $\nu_{15}$ , corresponding to the bending of the  $FSSF$  chain, was not observed, but was calculated to be  $57\text{ cm}^{-1}$ , higher than  $\nu_{19}$  as would be expected.

#### *The $b_1(a_{1u})$ Vibration*

The  $b_1$  vibration is inactive in both the infrared and Raman spectrum, and from the large moment of inertia of each  $SF_6$  group it would be expected to have a low frequency. Normally, the torsional frequency about a single bond is best obtained from thermodynamic data, but if one knows the geometrical barrier to overcome to allow a rotation about the bond it becomes possible to calculate the potential barrier hindering this rotation from a simple force constant method as proposed by Bäck (1). In  $S_2F_{10}$  the structure of lowest energy is most likely the staggered configuration  $D_{4d}$  in agreement

with the lowest energy structure  $D_{3d}$  in the ethane type molecules. To determine the potential barrier hindering rotation, it is assumed firstly that the closest approach of the two  $SF_6$  groups is limited by the repulsive forces of the opposed fluorine atoms on opposite groups, this being reasonable since the S—S bond length is 2.20 Å as compared with a normal S—S bond length of 2.05 Å in  $H_2S_2$  and 2.00 Å in  $S_2Cl_2$  (9), and secondly that during a rotation of the two  $SF_6$  groups from one staggered form to another, the F'F' distance between the two groups remains constant, which is consistent with the first assumption since the F'F' distance is the distance of closest approach. A simple calculation (see Appendix 2) gives the height of the potential barrier as  $V_{\max} = 2780$  cm.<sup>-1</sup>. This corresponds to a torsional frequency  $\nu_5 = 89$  cm.<sup>-1</sup>.

#### Vibrational Spectrum of Solid $S_2F_{10}$

The infrared spectrum of solid  $S_2F_{10}$  at liquid nitrogen temperatures was obtained in the hope that the crystal site symmetry may be such as to distinguish between the point groups  $D_{4h}$  and  $D_{4d}$  for the free molecule on the basis of the increase in the number of infrared active fundamentals and the removal of degeneracies.

However, in the observed spectrum from 1000 to 450 cm.<sup>-1</sup> (Fig. 3), nearly all the bands could be assigned to corresponding bands in the spectrum of the vapor or to combination bands with a lattice frequency of the order of 40 cm.<sup>-1</sup>, and only two bands at 894 and 683 cm.<sup>-1</sup> have been assigned to Raman active fundamentals  $\nu_1(a_1)$  and  $\nu_2(a_1)$  made infrared active by the crystal symmetry (Table IV). The intensity of  $\nu_2$  in the solid is surprising and probably arises owing to Fermi resonance with the infrared active fundamental  $\nu_7$ .

TABLE IV  
VIBRATIONAL ASSIGNMENT FOR SOLID  $S_2F_{10}$

Infrared, cm. <sup>-1</sup> (solid)	Infrared, cm. <sup>-1</sup> (vapor)	Raman, cm. <sup>-1</sup> (liquid)	Assignment
~526 sh	—	—	$\nu_{17} - 40 = 530$
537	—	—	—
~542	544	—	$\nu_{18}(e_1)$
568	—	—	—
570	571	—	$\nu_{17}(e_1)$
571 sh	—	—	—
580	—	—	$\nu_{18} + 40 = 580$
589	—	—	$\nu_{18} - 40 = 594$
602 sh	—	—	$\nu_{17} + 40 = 609$
610	—	—	—
~612	—	—	$\nu_{18} + 2 \times 40 = \begin{cases} 617 \\ 622 \end{cases}$
~656 sh	701	—	$\nu_8 - \nu_4 = 654$
~664 sh	—	—	$\nu_{12} + 40 = 674$
669	683	—	$\nu_7(b_2)$
682	—	690	$\nu_2(a_1)$ } Fermi resonance
770	—	—	$\nu_{16} - 40 = 766$
~795 sh	786	—	$\nu_4 + \nu_{18} = 786$
802	826	—	$\nu_{16}(e_1)$
806	—	—	—
819	—	—	$\nu_6 - 2 \times 40 = 820$
826	—	—	$\nu_{11} + \nu_{18} = 823$
842	—	—	$\nu_{16} + 40 = 846$
894	—	908	$\nu_1(a_1)$
900	938	—	$\nu_6(b_2)$
920	~915	—	$\nu_4 + \nu_7 = 922$
945	—	—	$\nu_6 + 40 = 940$
970	—	—	$\nu_6 + 2 \times 40 = 980$

The three type  $e_1$  infrared active bands of gaseous  $S_2F_{10}$  are split into two components in the solid, which verifies the assignment of these bands and suggests that the site symmetry of solid  $S_2F_{10}$  has a twofold axis at most. This lower site symmetry is also consistent with the assignment of the bands at 894 and 683  $cm^{-1}$  to  $\nu_1$  and  $\nu_2$  and the suggested Fermi resonance between  $\nu_2$  and  $\nu_7$ .

### Combination Bands

All the remaining bands in the infrared spectrum of  $S_2F_{10}$  vapor can be reasonably assigned to summation or difference tones of the fundamentals. Of these, only six bands needed explanation in terms of the three calculated fundamentals  $\nu_6$ ,  $\nu_{15}$ , and  $\nu_{19}$  and the agreement in each case was quite satisfactory.

In solid  $S_2F_{10}$  the remaining bands were assigned to combination tones of the fundamentals, but in this case it was considered necessary to include a lattice frequency at 40  $cm^{-1}$ , 11 bands being assigned satisfactorily as sum and difference tones of this frequency or its first overtone with the fundamentals. Of course,  $\nu_{19} = 37$   $cm^{-1}$  and  $\nu_5 = 89$   $cm^{-1}$  could have been used in place of the lattice frequency to account for the binary and ternary combinations, but the lattice mode was preferred since the bands assigned as combinations with its frequency did not occur in the vapor state.

### APPENDIX 1

The particular geometry of the  $S_2F_{10}$  molecule is such that the secular equation for the non-degenerate species containing an S—F' stretching mode can be factorized when a simple valence force potential function is assumed to describe the molecule. In such cases the SF' stretching mode factorizes out, simplifying the original secular equation for the species by one degree. If a more general valence force field is assumed to describe the molecule, this factorization can still be obtained if all interactions with the S—F' bond are assumed zero, except interactions between the SF' stretching of different bonds in the same  $SF'_4$  group.

For the  $S_2F_{10}$  molecule a valence force field was assumed to describe the molecule and it was made as general as was consistent with the number of observed frequencies by introducing suitably significant interactions in such a way that the factorizations mentioned above would still be possible.

The resulting valence force potential function was:

$$\begin{aligned}
 2V = & k_1 Q_{SS}^2 + k_2 (Q_{SF}^2 + Q_{SF'}^2) + 2g_1 (Q_{SF} + Q_{SF'}) Q_{SS} + k_3 r R (\delta_{FSS}^2 + \delta_{SSF'}^2) \\
 & + 2h_1 r R (\delta_{FSS} \delta_{SSF'}) + \sum_{i=1}^4 k_4 (Q_{SF'i}^2 + Q_{SF'i'}^2) + \sum_{i,j=1}^4 2g_2 (Q_{SF'i} Q_{SF'j} + Q_{SF'i'} Q_{SF'j'}) \\
 & + \sum_{i=1}^4 k_5 r^2 (\delta_{F'iSF'i+1}^2 + \delta_{F'i'SF'i+1'}^2) + \sum_{i=1}^4 k_6 r^2 (\delta_{F'SF'i}^2 + \delta_{F'SF'i'}^2) \\
 & + \sum_{i=1}^4 k_7 r^2 (\delta_{SSSF'i}^2 + \delta_{SSSF'i'}^2) + \sum_{i=1}^4 e_1 r (\delta_{F'SF'i} + \delta_{F'SF'i'}) Q_{SS} \\
 & + \sum_{i=1}^4 e_2 r (\delta_{SSSF'i} + \delta_{SSSF'i'}) Q_{SS}
 \end{aligned}$$

where the  $Q$ 's refer to bond extensions,  
the  $\delta$ 's refer to angle bendings,

S and  $\underline{S}$ , F and  $\underline{F}$  refer to the atoms in the different  $SF_5$  groups, and  $F'$  refers to an atom not on the fourfold axis, as defined in the footnote to Table I,

$r$  = S—F bond length,

$R$  = S—S bond length.

Proceeding in the usual manner, the secular equations

$$\det(FG - \lambda I) = 0$$

were set up for the different vibrational species. The terms in the symmetrical  $F$  and  $G$  matrices for the different symmetry species are given below. In all equations  $M$  = mass of S and  $m$  = mass of F.

The  $a_1(a_{1g})$  species

$$f_{11} = 8k_4 + 16g_2$$

$$f_{22} = 2k_2$$

$$f_{33} = k_1$$

$$f_{44} = 8k_6 + 8k_7$$

$$f_{12} = f_{13} = f_{14} = f_{24} = 0$$

$$f_{23} = 2g_1$$

$$f_{34} = 4e_1 - 4e_2$$

$$g_{11} = \frac{1}{8m}$$

$$g_{22} = \frac{1}{2M} + \frac{1}{2m}$$

$$g_{33} = \frac{2}{M}$$

$$g_{44} = \frac{1}{2M} + \frac{1}{8m}$$

$$g_{12} = g_{13} = g_{14} = 0$$

$$g_{23} = -\frac{1}{M}$$

$$g_{24} = -\frac{1}{2M}$$

$$g_{34} = \frac{1}{M}$$

The  $b_2(a_{2u})$  species

$$f_{11} = 8k_4 + 16g_2$$

$$f_{22} = 2k_2$$

$$f_{33} = 8k_6 + 8k_7$$

$$f_{12} = f_{13} = f_{23} = 0$$

$$g_{11} = \frac{1}{8m}$$

$$g_{22} = \frac{1}{2M} + \frac{1}{2m}$$

$$g_{33} = \frac{1}{2M} + \frac{1}{8m}$$

$$g_{23} = -\frac{1}{2M}$$

$$g_{12} = g_{13} = 0$$

The  $e_2$  species

$$(b_{1g}, b_{2u}) \begin{cases} f_{11} = 8k_4 - 16g_2 \\ f_{22} = 8k_6 + 8k_7 \end{cases}$$

$$(b_{1u}, b_{2g}) \begin{cases} f_{33} = 8k_5 \\ f_{12} = f_{13} = f_{23} = 0 \end{cases}$$

$$g_{11} = \frac{1}{8m}$$

$$g_{22} = \frac{1}{8m}$$

$$g_{33} = \frac{1}{2m}$$

$$g_{12} = g_{13} = g_{23} = 0$$



The  $e_1(e_u)$  species

$$\begin{aligned}
 f_{11} &= 4k_4 & g_{11} &= \frac{1}{2M} + \frac{1}{8m} \\
 f_{22} &= 4k_6 + \frac{R}{r}(2k_3 + 2h_1) & g_{22} &= \frac{1}{2M} + \frac{5}{8m} \\
 f_{33} &= 4k_7 + \frac{R}{r}(2k_3 + 2h_1) & g_{33} &= \frac{1}{8m} \\
 f_{44} &= 8k_5 & g_{44} &= \frac{1}{2M} + \frac{1}{8m} \\
 f_{23} &= \frac{R}{r}(2k_3 + 2h_1) & g_{12} = g_{14} &= -\frac{1}{2M} \\
 f_{12} = f_{13} = f_{14} = f_{24} = f_{34} &= 0 & g_{13} = g_{34} &= 0 \\
 & & g_{23} &= -\frac{1}{8m} \\
 & & g_{24} &= \frac{1}{2M}
 \end{aligned}$$

The  $e_3(e_g)$  species

$$\begin{aligned}
 f_{11} &= 4k_4 & g_{11} &= \frac{1}{2M} + \frac{1}{8m} \\
 f_{22} &= 4k_6 + (2k_3 - 2h_1)\frac{R}{r} & g_{22} &= \frac{1}{2M} + \frac{5}{8m} \\
 f_{33} &= 4k_7 \frac{r^2}{R^2} + (2k_3 - 2h_1)\frac{r}{R} & g_{33} &= \frac{2}{M} + \frac{1}{8m} \frac{R^2}{r^2} \\
 f_{44} &= 8k_5 & g_{44} &= \frac{1}{2M} + \frac{1}{8m} \\
 f_{23} &= 2k_3 - 2h_1 & g_{12} = g_{14} &= -\frac{1}{2M} \\
 f_{12} = f_{13} = f_{14} = f_{24} = f_{34} &= 0 & g_{13} &= -\frac{1}{M} \\
 & & g_{23} &= \frac{1}{M} - \frac{1}{8m} \frac{R}{r} \\
 & & g_{24} &= \frac{1}{2M} \\
 & & g_{34} &= \frac{1}{M}
 \end{aligned}$$

TABLE V  
CALCULATED VALENCE FORCE TYPE CONSTANTS FOR  $S_2F_{10}$

$k_1 = 2.806 \times 10^6$ dynes cm. <sup>-1</sup>	$g_1 = 0.406 \times 10^6$ dynes cm. <sup>-1</sup>
$k_2 = 5.582$ "	$g_2 = -0.164$ "
$k_3 = 0.162$ "	$h_1 = -0.118$ "
$k_4 = 5.602$ "	$e_1 - e_2 = -0.465$ "
$k_5 = 0.711$ "	
$k_6 = 0.711$ "	
$k_7 = 0.134$ "	

Using the equations derived above and the observed frequencies given in Table II, all the force constants and the three unknown frequencies  $\nu_{11}$ ,  $\nu_{15}$ , and  $\nu_{19}$  were calculated. The force constants are given in Table V.

Of interest is the good agreement between  $k_2$  and  $k_4$  (the SF and SF' stretching constant respectively), as would perhaps be expected. This excellent agreement indicated that the F'SF' bending constant could be made equal to  $k_6$ , the FSF' bending constant, and this was actually assumed.

## APPENDIX 2

Assuming the S<sub>2</sub>F<sub>10</sub> molecule to have the staggered configuration  $D_{4d}$ , then on rotation of one SF<sub>5</sub> group relative to the other the bonds and angles that are most likely to undergo a change are the SS bond and the FSF' and F'SS angles. Thus the potential barrier  $V_{\max}$  hindering rotation can be written after Bäck (1) as

$$\begin{aligned} [1] \quad V_{\max} &= \frac{1}{2}k_1Q_{SS}^2 + \frac{8}{2}(k_6+k_7)r^2\delta_{SSF'}^2 \\ &= \frac{1}{2}k_1Q_{SS}^2 + \frac{8}{2}Kr^2\delta_{SSF'}^2 \end{aligned}$$

where  $K = k_6 + k_7$ .

Consequently

$$[2] \quad dV_{\max} = 0 = k_1Q_{SS} \frac{dQ_{SS}}{d\delta_{SSF'}} + 8Kr^2\delta_{SSF'}.$$

Assuming that the F'F' distance between the two SF<sub>5</sub> groups is the same in the eclipsed configuration as in the staggered configuration,

$$[3] \quad 2Q_{SS} + 4r\delta_{SSF'} = \frac{\sqrt{2}r^2}{R}(\sqrt{2}-1).$$

Thus solving the three equations 1, 2, and 3 we obtain

$$V_{\max} = Kr^2 \left\{ \frac{K}{k_1} + \frac{1}{2} \right\} \frac{r^2}{R^2} (3-2\sqrt{2}) \left[ 1 + 4 \frac{K}{k_1} + 4 \left( \frac{K}{k_1} \right)^2 \right]^{-1}.$$

The torsional frequency corresponding to this potential barrier is given by

$$\nu_t = 2N \sqrt{V_{\max}/A}$$

where  $N$  = number of potential minima,

and  $A$  = rotational constant about the torsional axis.

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# THE ENTROPIES OF IONS IN AQUEOUS SOLUTION

## II. AN EMPIRICAL EQUATION FOR OXY-ANIONS<sup>1</sup>

A. M. COUTURE<sup>2</sup> AND K. J. LAIDLER

### ABSTRACT

The entropies of oxy-anions in aqueous solution are shown to obey the empirical relationship

$$\bar{S}_{\text{abs}}^0 = 40.2 + (3/2)R \ln M - 27.2 z^2 / 0.25nr$$

with a mean deviation of 3.6 e.u. In this equation  $\bar{S}_{\text{abs}}^0$  is the entropy relative to a value of  $-5.5$  e.u. for the proton,  $M$  is the molecular weight,  $z$  the number of charges on the ion,  $n$  the number of charge-bearing ligands,  $r$  is equal to  $r_{12} + 1.40$ , where  $r_{12}$  is the interatomic distance between the central atom and the surrounding oxygens, and  $1.40$  is the van der Waals radius of oxygen. The significance of the empirical equation is discussed.

### INTRODUCTION

In a recent paper (7), Part I of this series, it has been shown that the absolute entropies of ions (related to a value of  $-5.5$  e.u. for the proton) are accurately represented by the empirical equation

$$[1] \quad \bar{S}_{\text{abs}}^0 = 10.2 + (3/2)R \ln M - 11.6z^2/r_u.$$

Here  $M$  is the atomic weight,  $z$  the valency, and  $r_u$  the univalent radius as defined by Pauling (11). The applicability of the equation is almost, but not quite, as good if the ordinary crystal radii are employed. The equation is to be contrasted with other empirical equations, due to Powell and Latimer (13) and others (2, 3, 6), in which the entropy is related to  $z/r_e^2$ , where  $r_e$  is an effective radius obtained by the addition of a constant term to the crystal radii. The applicability of such equations is, in our view, fortuitous, arising from the choice of arbitrary entropies (based on a value of zero for the proton) and from the use of corrected radii. Our Equation [1] is consistent with Born's simple electrostatic model for ions in solution (1) although, for reasons to be discussed elsewhere (12), the coefficient of  $11.6$  is slightly but significantly different from that predicted by the Born equation.

In view of the applicability of equations involving  $z^2/r$  to the entropies of monatomic ions we are at present attempting to develop similar equations for polyatomic ions. The present paper is concerned with inorganic oxy-anions. The paper which follows (5) deals with the partial molal volumes of these ions, following a treatment recently proposed (4) for the volumes of monatomic ions.

### THE DATA

The conventional partial molal entropies of a number of oxy-anions (10), based on a value of zero for the proton, are shown in the second column of Table I. These have been converted into absolute entropies by the addition of  $5.5 |z_-|$ , where  $|z_-|$  is the number of negative charges on the ion, and the results are shown in the third column.

Also shown in the table are the values of  $r_{12}$ , the distance between the center of the central atom and the center of the surrounding oxygen atoms; these values have been

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TABLE I  
 CONVENTIONAL AND ABSOLUTE ENTROPIES OF OXY-ANIONS

Ion	$S_{\text{conv}}^0$ (e.u.)	$S_{\text{abs}}^0$ (e.u.)	Interatomic distance ( $r_{12}$ ) (Å)	$r$ (Å)	$S_{\text{abs}}^0$ $-(3/2)R \ln M$	$0.25nr$	$\frac{z^2}{0.25nr}$
$\text{ClO}^-$	10.0	15.5	1.70	3.10	3.8	0.77	1.30
$\text{NO}_2^-$	29.9	35.4	1.24	2.64	24.0	1.32	0.76
$\text{BO}_2^-$	20	25.5	1.37	2.77	14.3	1.38	0.72
$\text{ClO}_2^-$	24.1	29.6	1.52	2.92	17.1	1.46	0.68
$\text{AlO}_2^-$	25	30.5	1.54	2.94	18.4	1.47	0.68
$\text{HCO}_2^-$	22.7	28.2	1.26	2.66	16.0	1.33	0.75
$\text{HSO}_2^-$	26	31.5	1.39	2.79	18.4	1.39	0.72
$\text{HSeO}_2^-$	30.4	35.9	1.63	3.03	21.5	1.51	0.66
$\text{H}_2\text{PO}_4^-$	21.3	26.8	1.55	2.95	13.2	1.47	0.68
$\text{H}_2\text{AsO}_4^-$	28	33.5	1.75	3.15	18.8	1.57	0.64
$\text{NO}_3^-$	35.0	40.5	1.24	2.64	28.2	1.98	0.50
$\text{ClO}_3^-$	39.0	44.5	1.48	2.88	31.3	2.16	0.46
$\text{BrO}_3^-$	38.5	44.0	1.68	3.08	29.6	2.38	0.43
$\text{HSO}_4^-$	30.3	35.8	1.50	2.90	22.2	2.17	0.46
$\text{ClO}_4^-$	43.2	48.7	1.52	2.92	35.0	2.92	0.34
$\text{MnO}_4^-$	45.4	50.9	1.69	3.09	36.7	3.09	0.32
$\text{ReO}_4^-$	50	55.5	1.90	3.30	39.1	3.30	0.30
$\text{CO}_3^{--}$	-12.7	-1.7	1.26	2.66	-13.9	1.99	2.01
$\text{SO}_3^{--}$	-7	4.0	1.39	2.79	-9.1	2.09	1.91
$\text{SeO}_3^{--}$	3.9	14.9	1.70	3.10	0.5	2.32	1.72
$\text{HPO}_4^{--}$	-8.6	2.4	1.55	2.95	-11.2	2.21	1.81
$\text{HAsO}_4^{--}$	0.9	11.9	1.75	3.15	-2.8	2.36	1.69
$\text{SO}_4^{--}$	4.1	15.1	1.50	2.90	1.5	2.90	1.38
$\text{SeO}_4^{--}$	5.7	16.7	1.65	3.05	1.9	3.05	1.31
$\text{CrO}_4^{--}$	9.2	20.2	1.60	3.00	6.1	3.00	1.33
$\text{MoO}_4^{--}$	14	25.0	1.83	3.23	9.9	3.23	1.24
$\text{WO}_4^{--}$	15	26.0	1.95	3.35	9.6	3.35	1.19
$\text{PO}_4^{---}$	-52.0	-35.5	1.55	2.95	-49.1	2.95	3.06
$\text{AsO}_4^{---}$	-34.6	-18.1	1.75	3.15	-32.8	3.15	2.86

derived from Pauling's covalent radii (11). The fourth column of Table I shows the values of  $r_{12}+1.40$ ; since 1.40 Å is the van der Waals radius of oxygen the distance  $r_{12}+1.40$  represents the radius of a sphere that completely circumscribes the anion.

#### AN EMPIRICAL EQUATION

An inspection of Table I reveals that the entropy decreases as the charge increases, but increases as the interatomic distance and the number of charge-bearing ligands increase. Further examination shows that the entropy shows a dependence on  $z^2/r$ , where  $r = r_{12}+1.40$ . Fig. 1 shows a plot of  $\bar{S}_{\text{abs}}^0$  against  $z^2/r$ , and it is seen that the points are grouped according to the number of charge-bearing ligands,  $n$ . There is no grouping in terms of the total number of ligands.

Since it is the number of charge-bearing ligands that is important, it follows that the distribution of charges plays an important role. An attempt was made to correlate the entropies with dipole moments as well as with  $z^2$ , but this proved unsuccessful. One can only make estimates of the dipole moments of ions, but one knows that the moments for certain symmetrical ions (e.g.  $\text{SO}_4^{--}$ ,  $\text{PO}_4^{--}$ ,  $\text{NO}_3^-$ ) must be zero. Even for these ions of zero moment there is still a grouping with respect to the number of charge-bearing ligands. More is therefore involved than the dipole moment.

The groups corresponding to the different values of  $n$  can be brought together if the

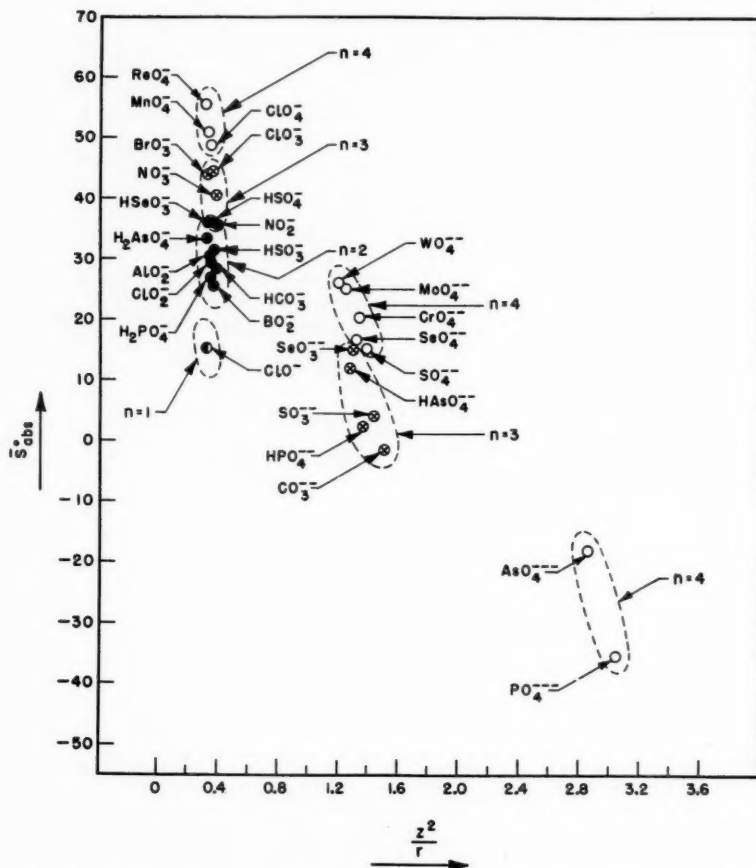


FIG. 1. A plot of  $\bar{S}^0_{abs}$  against  $z^2/r$ , where  $r$  is equal to  $r_{12} + 1.40$ . The points are seen to be grouped according to the number of charge-bearing ligands,  $n$ .

effective radius  $r$  ( $=r_{12} + 1.40$ ) is multiplied by  $n$ : in other words, if the entropies are plotted against  $z^2/rn$ . As with the monatomic ions, the correlation is improved if one subtracts from the entropies the quantity  $(3/2)R \ln M$ , where  $M$  is the molecular weight. This term, as discussed in Part I (7), is related to the non-electrostatic contribution to the entropy. Values of  $\bar{S}^0_{abs} - (3/2)R \ln M$  are shown in Table I, and are plotted against  $z^2/0.25nr$  (also listed in Table I) in Fig. 2. The use of  $z^2/0.25nr$  instead of  $z^2/nr$  is purely a matter of convenience. For ions like  $SO_4^{--}$ , for which  $n$  is 4,  $z^2/0.25nr$  becomes  $z^2/r$ , while  $r$  is correspondingly reduced for values of  $n$  of less than 4.

The points in Fig. 2 are seen to lie close to a straight line. By the method of least squares the equation of the line was found to be

$$[2] \quad \bar{S}^0_{abs} = 40.2 + (3/2)R \ln M - 27.2 z^2/0.25nr$$

with a mean deviation of 3.6 e.u.



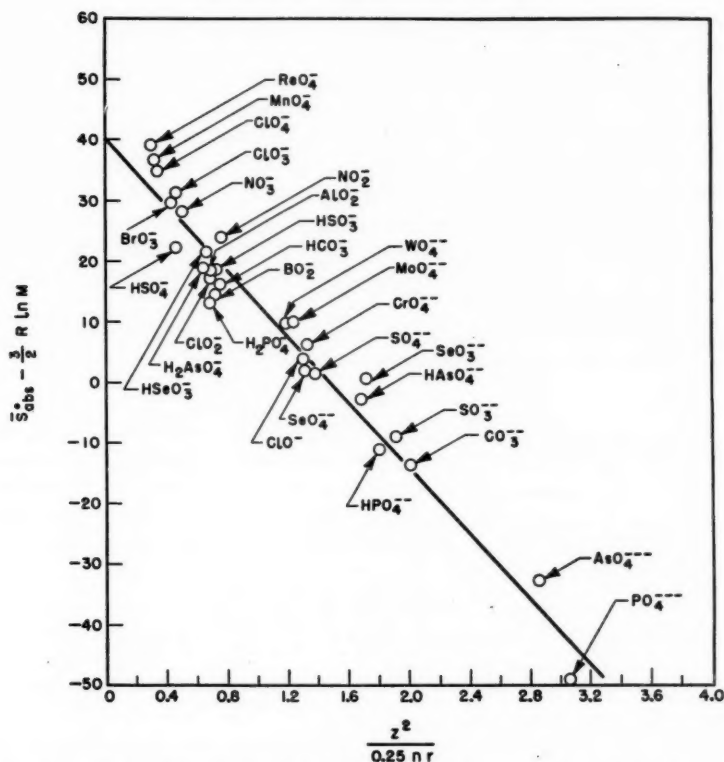


FIG. 2. A plot of  $S^\circ_{\text{abs}} - (3/2)R \ln M$  against  $z^2/0.25nr$ . The mean deviation from the straight line is 3.6 e.u.

The use of  $r_{12}$  in place of  $r$  was also investigated, but the correlation was then not quite as satisfactory.

#### DISCUSSION

Equation [2] is seen to be of the same general form as Eq. [1], which was obtained for monatomic ions. It again consists of a non-electrostatic part ( $40.2 + (3/2)R \ln M$ ) and an electrostatic part, the final term. The correlation is again with  $z^2$  rather than with  $z$ .

The relationships expressed in Eq. [2] may be explained on the basis of a very simple model. The ions with four charge-bearing ligands may conveniently be regarded as standard, and for them  $0.25nr$  represents the radius of the circumscribing sphere. If, for example,  $n$  is 2, the radius appearing in the denominator,  $0.25nr$ , is one half the radius of the circumscribing sphere; the behavior of such an ion (as far as entropy is concerned) is therefore equivalent to that of an ion having half the radius of the circumscribing sphere. This is not surprising, since for such an ion the water molecules have much more access to the charge-bearing centers.

The fact that it is the number of charge-bearing ligands that counts, and not the total number of ligands, is of some special interest and significance. As far as the electrostatic contribution to the entropy is concerned it is evidently only the total charge and the

distribution of charges that are important. For the ions under consideration in the present paper a non-charge-bearing ligand can be only an OH group, and the empirical equation implies that the presence or absence of an OH group is immaterial as far as entropy is concerned. That this is really the case from the experimental point of view is revealed by an inspection of Figs. 1 and 2 in which it may be seen, for example, that the ions  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HSO}_3^-$ , and  $\text{ClO}_2^-$ , with very similar  $z^2/r$  values, have almost identical entropies; this is so in spite of the fact that the ions contain 2, 1, and 0 non-charge-bearing ligands (OH) respectively. These OH groups will, of course, behave very much like the OH groups in the surrounding water molecules. It is true that they should contribute some non-electrostatic entropy, but such a contribution is very small and is partly taken into account in the  $(3/2)R \ln M$  term.

Subsequent papers will deal with the entropies of other complex ions and with the application of the present conclusions to kinetic problems (8, 9).

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# THE PARTIAL MOLAL VOLUMES OF IONS IN AQUEOUS SOLUTION

## II. AN EMPIRICAL EQUATION FOR OXY-ANIONS<sup>1</sup>

A. M. COUTURE<sup>2</sup> AND K. J. LAIDLER

### ABSTRACT

The partial molal volumes of oxy-anions, obtained from density data, have been correlated with the radius, the charge, and the number of ligands of the ions. The volumes relative to a value of  $-6.0$  ml. for the proton are represented by the equation:

$$\bar{V}'_- = 58.8 + 0.89r^3 - 26|z_-|$$

where  $r$  and  $z_-$  have the same significance as in the preceding paper on entropies. The equation is compared with the one for monatomic ions, and the significance of the effective radius  $r$  is discussed.

### INTRODUCTION

It has recently been shown (1) that partial molal volumes of monatomic ions in aqueous solution can be expressed as a simple function of the charge and the crystal radius. This correlation suggested that, as it is the case with entropies (2), a similar situation might exist for more complex ions. The present communication is therefore concerned with obtaining such an empirical equation for oxy-anions.

### EMPIRICAL EQUATION

The equation proposed (1) to correlate the partial molal volumes of all monatomic cations and anions is

$$[1] \quad \bar{V}'_{\pm} = 16 + 4.9r^3 - 26|z_{\pm}|$$

where  $\bar{V}'_{\pm}$  refers to volumes based on a value of  $-6.0$  ml. for  $\bar{V}'_{H^+}$ ,  $r$  is the Goldschmidt crystal radius (3), and  $|z_{\pm}|$  the absolute value of the charge. An interpretation of this equation was given: the first two terms are considered to be related to the intrinsic volume of the ion, and the final term to the electrostriction of the water molecules surrounding the ion.

The same terms should also appear in the volume of the oxy-anions. These volumes, both on the scale of  $\bar{V}_{H^+} = 0$  and  $\bar{V}'_{H^+} = -6.0$  ml., are listed in Table I; the volumes have been calculated from density data (4) and agree with the few values given by Owen and Brinkley (5). The problem with oxy-anions is to define a suitable effective radius and to elucidate the effect of charge-bearing ligands. Since the use of  $0.25nr$  (where  $n$  is the number of charge-bearing ligands and  $r$  the sum of the Pauling (6) interatomic distance,  $r_{12}$ , and the van der Waals radius of the oxygen atom) was very suitable in the case of entropies (2), we have attempted to employ it here as an effective radius. These values of  $0.25nr$  are also included in Table I. From the study of the variation of the volumes with the cube of this radius and with the charge, we arrived at the following equation for the volume related to the value of  $-6.0$  ml. for the proton:

$$[2] \quad \bar{V}'_- = 58.8 + 0.89(0.25nr)^3 - 26|z_-|.$$

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Contribution from the Department of Chemistry, University of Ottawa, Ottawa, Canada.

<sup>2</sup>Holder of a Scholarship from the Ontario Research Foundation.

TABLE I  
 PARTIAL MOLAL VOLUMES AND EFFECTIVE RADII OF OXY-ANIONS

Ion	$\bar{V}'_{\text{conv}}$	$\bar{V}'$	$r_{12}$	$0.25nr$	Source of $\bar{V}'_{\text{conv}}$
$\text{NO}_3^-$	26.5	32.5	1.24	1.32	From $\text{NaNO}_3$ and $\text{KNO}_3$
$\text{H}_2\text{PO}_4^-$	29.4	35.4	1.55	1.47	From $\text{NaH}_2\text{PO}_4$ and $\text{KH}_2\text{PO}_4$
$\text{H}_2\text{AsO}_4^-$	35.5	41.5	1.75	1.57	From $\text{NaH}_2\text{AsO}_4$
$\text{HCO}_3^-$	23.5	29.5	1.26	1.33	From $\text{NaHCO}_3$ , $\text{KHCO}_3$ , and (5)
$\text{ClO}_3^-$	36.4	42.4	1.48	2.16	From $\text{LiClO}_3$ , $\text{NaClO}_3$ , $\text{KClO}_3$ , and (5)
$\text{BrO}_3^-$	35.6	41.6	1.68	2.38	From $\text{NaBrO}_3$ , $\text{KBrO}_3$ , and (5)
$\text{HSO}_4^-$	31.4	37.4	1.50	2.17	From $\text{NaHSO}_4$ , $\text{KHSO}_4$ , $\text{H}_2\text{SO}_4$ , and (5)
$\text{HSeO}_4^-$	31.4	37.4	1.65	2.29	From $\text{H}_2\text{SeO}_4$
$\text{NO}_2^-$	29.3	35.3	1.24	1.98	From $\text{HNO}_3$ , $\text{KNO}_3$ , and (5)
$\text{SO}_3^{--}$	9.5	21.5	1.39	2.09	From $\text{Na}_2\text{SO}_3$ and $\text{K}_2\text{SO}_3$
$\text{HPO}_4^{--}$	8.3	20.3	1.55	2.21	From $\text{Na}_2\text{HPO}_4$
$\text{CO}_3^{--}$	-1.7	10.3	1.26	1.99	From $\text{Na}_2\text{CO}_3$ , $\text{K}_2\text{CO}_3$ , and (5)
$\text{ClO}_4^-$	46.4	52.4	1.52	2.92	From $\text{HClO}_4$ , $\text{NaClO}_4$ , and $\text{NH}_4\text{ClO}_4$
$\text{MnO}_4^{--}$	43.2	49.2	1.69	3.09	From $\text{KMnO}_4$ and (5)
$\text{SO}_4^{--}$	16.4	28.4	1.50	2.90	From $\text{Li}_2\text{SO}_4$ , $\text{K}_2\text{SO}_4$ , $(\text{NH}_4)_2\text{SO}_4$ , and (5)
$\text{SeO}_4^{--}$	21.5	33.5	1.65	3.05	From $\text{Na}_2\text{SeO}_4$ and $\text{K}_2\text{SeO}_4$
$\text{CrO}_4^{--}$	20.3	32.3	1.60	3.00	From $\text{Li}_2\text{CrO}_4$ , $\text{Na}_2\text{CrO}_4$ , $\text{K}_2\text{CrO}_4$ , and (5)
$\text{MoO}_4^{--}$	29.5	41.5	1.83	3.23	From $\text{Na}_2\text{MoO}_4$ and $\text{K}_2\text{MoO}_4$
$\text{WO}_4^{--}$	26.3	38.3	1.95	3.35	From $\text{Na}_2\text{WO}_4$ and $\text{K}_2\text{WO}_4$
$\text{AsO}_4^{--}$	-14.9	3.1	1.75	3.15	From $\text{Na}_2\text{AsO}_4$

A plot of  $\bar{V}'_- + 26|z_-|$  versus  $(0.25nr)^3$  appears in Fig. 1 and the mean deviation in the volume is 3.5 ml. The corresponding equation for  $\bar{V}'_-$  (related to zero for the proton) is

$$[3] \quad \bar{V}'_- = 58.8 + 0.89 (0.25nr)^3 - 32|z_-|.$$

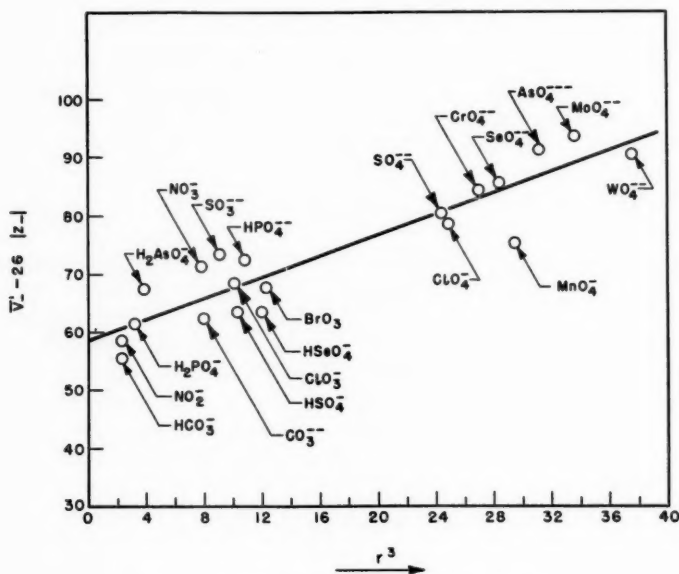


FIG. 1. A plot of  $\bar{V}'_- + 26|z_-|$  against  $(0.25nr)^3$ .

## DISCUSSION

Although the radius ( $r = r_{12} + 1.40$ ) is corrected empirically to take into account the effect of the charge-bearing ligands, the effective radius thus obtained is easily visualized. The ion with four charge-bearing ligands is taken as the standard and its effective radius is  $r$ . As the number of charge-bearing ligands decreases the effective radius is reduced in the same proportion; hence

$$\begin{aligned} r_e &= \frac{3}{4}r \text{ if } n = 3, \\ r_e &= \frac{1}{2}r \text{ if } n = 2, \\ r_e &= \frac{1}{4}r \text{ if } n = 1. \end{aligned}$$

The ligands ( $-\text{OH}$ ) which cannot have a charge are discarded as they make no more contribution to the volume than if they belonged to the water molecules surrounding the ion.

An effective radius may be calculated by considering only the volumes of the atoms involved, i.e.

$$[4] \quad r_{\text{calc}} = \sqrt[3]{r_{\text{covalent}}^3 (\text{central atom}) + n(1.40)^3}$$

(where  $1.40 \text{ \AA}$  is the van der Waals radius of O). If this  $r_{\text{calc}}$  and the  $r$  obtained empirically are compared, they are found to agree very closely for  $n = 3$ ;  $r_{\text{calc}}$  is smaller than  $r$  when  $n = 4$  but is larger when  $n = 2$  or  $1$ . These differences arise in part from the uncertainty in the radii of the atoms combined to form oxy-anions owing to a certain amount of interpenetration. Moreover, depending on the number of atoms involved, there is some dead space unavailable to water molecules, and this dead space is included in  $r$  but not in  $r_{\text{calc}}$ .

It is interesting to note that the coefficient of  $|z|$  is the same in Equation [2] as in Equation [1]. The  $|z|$  term is related in both cases to the electrostriction of the water molecules in the neighborhood of the ion, and the fact that two empirical equations, obtained independently for two types of ions, agree in the coefficient of this term is very probably more than a coincidence: it is an indication that the scale on which the volumes are based is an absolute scale and hence that  $-6.0 \text{ ml.}$  is the true partial molal volume of the proton. On the scale where  $\bar{V}_{\text{H}^+} = 0$ , the coefficient of  $|z|$  is  $-20$  for monatomic cations but  $-32$  for oxy-anions. The coefficient of  $|z|$  for the monatomic anions should also be  $-32$ , which it is not (it is  $-20$ ). However, it must be pointed out that all the monatomic anions are univalent with the exception of  $\text{S}^{2-}$ , so that the accuracy of the slope in a plot of  $(\bar{V} - 4.9r^3)$  against  $|z|$  depends solely on the accuracy of the volume of  $\text{S}^{2-}$ ; if it were not for  $\text{S}^{2-}$  the slope, which is the coefficient of  $|z|$ , could have any value. There are several reasons for doubting the accuracy of  $\bar{V}_{\text{S}^{2-}}$ : (1) it is derived from the partial molal volume of only one solute,  $\text{Na}_2\text{S}$ ; (2) if an attempt is made to bring together monatomic cations and anions,  $\text{S}^{2-}$  does not agree with the general equation, thus leading to the conclusion that this equation applies only to monatomic cations and univalent monatomic anions; (3) the equation for oxy-anions points to a dependence on  $-26|z_-|$  for  $\bar{V}'$  and on  $-32|z_-|$  for  $\bar{V}$ , and all monatomic anions except  $\text{S}^{2-}$  can be made to fit such a dependence. The evidence thus points to  $-6.0 \text{ ml.}$  as the absolute volume of the proton.

The coefficients of  $r^3$  do not correspond, but this was not expected since the two  $r$ 's are different, one being the crystal radius, and the other being derived empirically.

## ACKNOWLEDGMENT

One of us (A.M.C.) wishes to thank the Ontario Research Foundation for the award of a Scholarship.

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## LYCOPODIUM ALKALOIDS

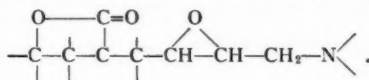
### V. OXIDATION AND REDUCTION STUDIES ON ANNOTININE AND ITS DERIVATIVES<sup>1</sup>

E. E. BETTS<sup>2</sup> AND DAVID B. MACLEAN

#### ABSTRACT

Annotinine lactam  $C_{16}H_{19}O_4N$  has been converted by the action of dilute sulphuric acid to the lactamdol,  $C_{16}H_{21}O_3N$ . Oxidation studies on the lactamdol have confirmed the presence of the epoxide ring in the alkaloid and have established the six-membered character of the lactam ring. The allylamine structure of unsaturated lactone A,  $C_{16}H_{21}O_2N$ , has been confirmed and a number of intermediate oxidation products of this compound have been isolated and characterized. Raney nickel reduction of annotinine yielded hydroxy annotinine,  $C_{16}H_{23}O_3N$ , and saturated lactone A,  $C_{16}H_{23}O_2N$ . Catalytic reduction of annotinine lactam over Adams' catalyst in acidic medium converted it partially to annotinine.

Annotinine,  $C_{16}H_{21}O_3N$ , is the major alkaloid of *Lycopodium annotinum* L. Because of its availability and reactivity the chemistry of this alkaloid has been studied more intensively than others of the *Lycopodium* group. Annotinine contains a tertiary nitrogen, an oxide ring, a lactone ring, and a combination of four carbocyclic and heterocyclic rings (8). An epoxide ring structure and its relationship to the nitrogen atom was proposed by MacLean and Prime (7) and has been supported by the work of Anet and Marion (1) and of Wiesner *et al.* (4). The lactone ring is apparently a  $\gamma$ -lactone from its infrared spectrum (9). Wiesner *et al.* (5) have related the position of the lactone ring to the other functions in the molecule. These relationships can be expressed in the following manner:



Evidence for the size and nature of the four principal rings in the molecule has been obtained by infrared spectroscopy and by dehydrogenation experiments. The infrared spectrum of annotinine lactam,  $C_{16}H_{19}O_4N$ , has suggested that the nitrogen-containing ring carrying the epoxide function is six-membered, although the possibility of a larger ring is not excluded (9). Similarly, when the secondary hydroxyl group derived from the lactone function was converted to a ketone, the infrared spectrum indicated that the ring bearing this function was six-membered or larger (10). A series of dehydrogenation studies on annotinine and its derivatives has been carried out by Wiesner and his associates. By a careful characterization of the products of these reactions and an exceptionally clever interpretation of their origin, they have proposed several plausible structures for the alkaloid (10, 12, 13).

There is still lacking, however, unequivocal chemical confirmation of many of the structural features of the molecule even to the size of the oxide and lactone rings. Furthermore, it has never been established that derivatives of annotinine which have been used in dehydrogenation studies have not suffered rearrangements in the course of their preparation. In this communication we present good evidence for the presence of the epoxide function and for the six-membered character of the nitrogen ring carrying this

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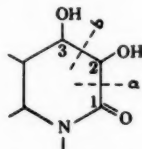
function. In the course of our work we also had occasion to examine some reactions of unsaturated lactone A (8, 9) and wish to report in particular on some oxidation studies on this compound. Annotinine derivatives used in dehydrogenation studies have been related to annotinine, thus precluding the possibility of rearrangement in their preparation. Finally, and as a matter of interest, we have been able to convert annotinine lactam to annotinine.

Annotinine,  $C_{16}H_{21}O_3N$  (I), has been converted in good yield into annotinine lactam,  $C_{16}H_{19}O_4N$  (II) (7). Treatment of II with boiling aqueous sulphuric acid converted it to annotinine lactamdiol,  $C_{16}H_{21}O_5N$  (III), which should contain the following arrangement

of groups:  $\text{>N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CHOH}-\text{CHOH}-$ . It would be expected to react readily with glycol cleavage reagents. However, periodate did not react, but lead tetraacetate slowly oxidized the molecule with consumption of 3 moles of the reagent. Two moles of reagent would be consumed in cleavage and the third in oxidation of the liberated formic acid. Oxidation of III with potassium permanganate in acetic acid or with chromic acid in glacial acetic acid converted it in low yield into two products, one neutral and one acidic. The neutral product  $C_{15}H_{17}O_4N$  (IV) had three strong absorption bands in the carbonyl region of the infrared at  $1708\text{ cm}^{-1}$ ,  $1760\text{ cm}^{-1}$ , and  $1780\text{ cm}^{-1}$  corresponding respectively to a  $\gamma$ -lactam, a five-membered cyclic ketone, and a lactone ring. Treatment of IV with sodium borohydride in ethanol converted it to  $C_{15}H_{19}O_4N$  (V), which now had two bands in the carbonyl region of the infrared at  $1682\text{ cm}^{-1}$  corresponding to a  $\gamma$ -lactam and at  $1780\text{ cm}^{-1}$  to a  $\gamma$ -lactone. The band at  $1760\text{ cm}^{-1}$  had disappeared and a new band at  $3335\text{ cm}^{-1}$  in the hydroxyl region had appeared. The formation of the  $\gamma$ -lactam with loss of a single carbon supports the proposal of a six-membered nitrogen ring at this site.

The acidic fraction  $C_{15}H_{19}O_5N$  (VI) had three peaks in the carbonyl region of the infrared at  $1610\text{ cm}^{-1}$ ,  $1705\text{ cm}^{-1}$ , and  $1775\text{ cm}^{-1}$  attributed to amide, carboxylic acid, and  $\gamma$ -lactone functions respectively. Hydrolysis of VI with dilute sulphuric acid yielded formic acid in equimolar amount and the amino acid  $C_{14}H_{19}O_4N$  (VII), identified through its methyl ester, previously reported by Anet and Marion (1) and by Wiesner (4). Compound VI is obviously the N-formyl derivative of amino acid VII. The low yield of IV and VI is likely due to the concomitant formation of amino acid VII, and indeed, its presence has been detected.

The formation of these products can be explained with the aid of the accompanying partial formula.

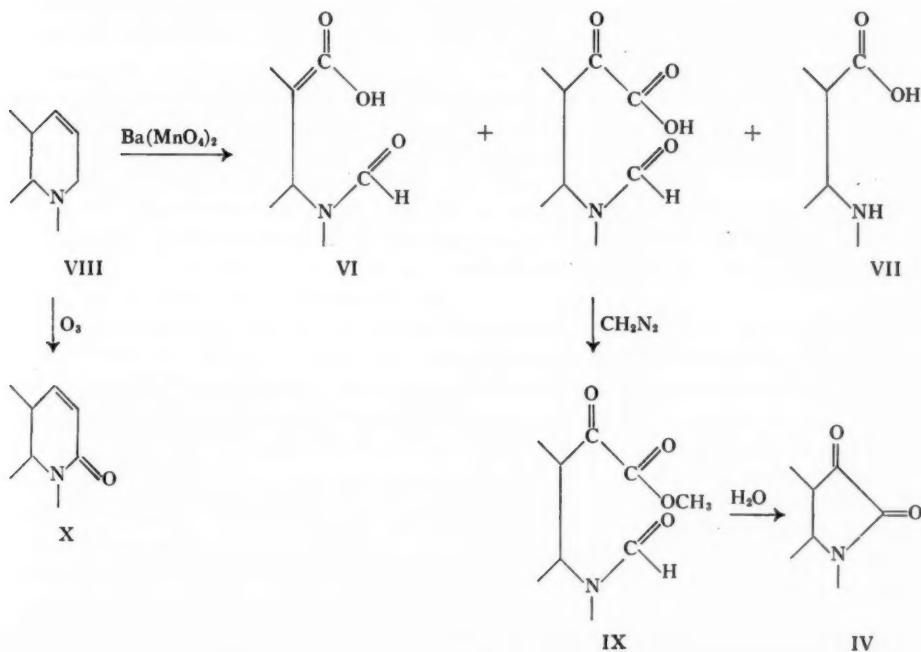


An initial fission of the system at (a) would yield a carbamic acid which would lose  $\text{CO}_2$  to yield the secondary amine. Oxidation of center 3 would yield an  $\alpha$ -keto acid which by cyclization would yield IV. Fission at (b) followed by oxidation at each center would form an N-oxalyl carboxylic acid which in the medium would decarboxylate to VI. Either IV or VI or their progenitors would yield VII by hydrolysis or oxidation or a combination of the two.

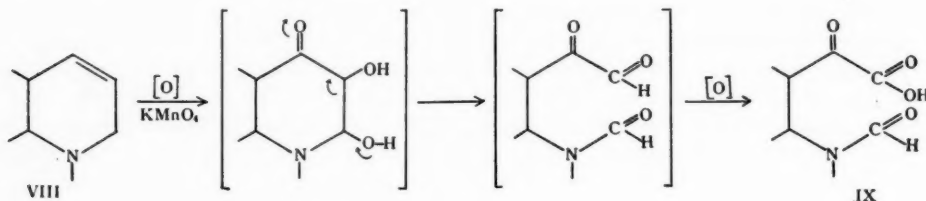
The compound designated unsaturated lactone A,  $C_{16}H_{21}O_2N$  (VIII), has been assigned an allylamine structure by Anet and Marion on the basis of its origin and a comparison of its  $pK_a$  with that of its dihydro derivative (1). A compound of this structure would be expected to react readily with cyanogen bromide. However, VIII was recovered in 80% yield or better when it was treated with cyanogen bromide under a variety of experimental conditions. Because of this anomalous result we decided to reinvestigate the composition of two products of the barium permanganate oxidation of VIII isolated some years ago. One of these compounds,  $C_{16}H_{19}O_6N$ , proved to be identical with VI. The second compound, isolated as its methyl ester,  $C_{17}H_{21}O_6N$  (IX), had four bands in the carbonyl region of the infrared. A double peak at  $1633\text{ cm}^{-1}$  and  $1645\text{ cm}^{-1}$  was assigned to an amide function while bands at  $1710\text{ cm}^{-1}$ ,  $1743\text{ cm}^{-1}$ , and  $1780\text{ cm}^{-1}$  were assigned to keto carbonyl, carbomethoxy, and  $\gamma$ -lactone functions respectively. Hydrolysis of IX with dilute sulphuric acid yielded formic acid and a trace of compound IV, thereby establishing the structure of IX. The amino acid VII is the major oxidation product as already established by Anet and Marion (1).

The formation of formyl derivatives on oxidation, coupled with its inertness toward cyanogen bromide, suggested that VIII might contain a vinylamine rather than an allylamine structure. To clarify this point VIII was treated with ozone. Ozonolysis of a vinylamine should yield an N-formyl derivative while an allylamine would be expected to yield an amino dicarboxylic acid. The reaction took neither course, but instead yielded the conjugated lactam,  $C_{16}H_{19}O_3N$  (X), previously isolated by MacLean and Prime (7) and by Anet and Marion (1). The formation of X can be rationalized more readily from an allylamine structure than from the alternative vinylamine formulation.

The several oxidation products are depicted by the partial formulas below:



The formation of X can be accommodated by formation of a hydroperoxide at the methylene carbon and its subsequent decomposition. If we assume that X is an intermediate in the permanganate oxidation, then VI could arise by hydroxylation of X followed by cleavage as indicated previously in its derivation from III. The amino acid VII is the product of complete oxidation and hydrolysis. The formation of X can be accounted for by the following sequence:<sup>3</sup>



Two derivatives of annotinine which have been used in dehydrogenation studies are the amino acid VII (1, 11) and the methyl ester derived from anhydro annotinine lactam chlorohydrin (XI) (12, 13). Compound XI was readily oxidized to VII, which in turn was also prepared from VIII. Both VIII and XI were formed by dehydration reactions in acid media where a rearrangement of the carbon skeleton of annotinine was possible, if not probable. We have now established that VIII and therefore XI have the same skeletal structure as the parent alkaloid. Annotinine was reduced with hydrogen over Raney nickel to yield two products,  $C_{16}H_{23}O_3N$  (XII) and  $C_{16}H_{23}O_2N$  (XIII). Compound XII was hydroxy annotinine formed by fission of the oxide ring, while XIII resulted from complete removal of the oxide ring and was identical with the dihydro derivative of VIII. The isolation of XIII indicates that the original skeletal arrangement of annotinine is preserved in both VIII and XI.

A method of converting annotinine lactam to annotinine was accidentally discovered in the course of some experiments on alternate methods of preparation of hydroxy annotinine lactam (XIV) (7). Reduction of the lactam II over platinum catalyst in neutral or in basic medium yielded XIV. In the presence of small amounts of hydrochloric acid, annotinine and annotinine lactam chlorohydrin were recovered. The formation of the chlorohydrin requires no comment while the unusual reduction is most likely a peculiarity of the  $\alpha,\beta$ -epoxy lactam system.

#### EXPERIMENTAL

##### *Preparation of Annotinine Lactamdiol, $C_{16}H_{21}O_5N$ (III)*

Annotinine lactam (2 g.) was refluxed overnight with 40 ml. of 10% sulphuric acid containing a few drops of dioxane to facilitate solution. The dioxane was boiled off, and the solution was cooled, made alkaline with ammonium hydroxide, and extracted four times with chloroform. The combined chloroform extracts were dried over sodium sulphate and then taken to dryness. The residue (1.64 g.) was recrystallized from acetone and melted at 238–239° C.<sup>4</sup>

Calc. for  $C_{16}H_{21}O_5N$ : C, 62.54; H, 6.84; N, 4.56%. Found: C, 62.89, 62.78; H, 6.75, 6.82; N, 4.76%.

<sup>3</sup>We are indebted to the referee for suggesting this mechanism for the formation of compound X.

<sup>4</sup>All melting points are corrected.

The infrared spectrum<sup>5</sup> (nujol) had two bands in the hydroxyl region at 3530  $\text{cm}^{-1}$  (sharp) and 3300  $\text{cm}^{-1}$  (broad), one in the lactone region at 1770  $\text{cm}^{-1}$ , and one in the lactam region at 1620  $\text{cm}^{-1}$ .

*Treatment of Annotinine Lactamdiol with Lead Tetraacetate*

Annotinine lactamdiol (0.1537 g.) was dissolved in 50 ml. of aldehyde-free glacial acetic acid and mixed with 50 ml. of 0.1472 *N* lead tetraacetate in glacial acetic acid. Aliquots were removed at regular intervals and added to 20 ml. of buffer solution containing 5 g. of potassium iodide and 62.5 g. of sodium acetate per 250 ml. of solution according to the procedure of Hackett and McClenahan (3). The excess iodine was titrated with standard sodium thiosulphate solution. A blank solution was run concurrently. The results are tabulated below.

Time in hours	Mole ratio of $\text{Pb}(\text{OAc})_4$ consumed
24	0.35
48	0.79
72	1.17
91	1.48
117	1.94
143	2.33
167	2.65
191	2.84
215	3.06
238	3.10

*Chromic Acid Oxidation of Annotinine Lactamdiol (III)*

A solution of 0.30 g. of annotinine lactamdiol in 5 ml. of glacial acetic acid was warmed to 60° and a solution of chromic acid in glacial acetic acid was added until the yellow color persisted. Excess oxidant was destroyed with methanol and the solution evaporated to dryness under reduced pressure. The residue was dissolved in water, made alkaline with ammonia, and extracted with chloroform. The chloroform extracts were washed with acid, dried over sodium sulphate, and evaporated to dryness. The residue, after several recrystallizations from ether, melted at 197–199° C.

Calc. for  $\text{C}_{15}\text{H}_{17}\text{O}_4\text{N}$ : C, 65.49; H, 6.23%. Found: C, 65.92, 65.79; H, 6.23, 6.24%.

The infrared spectrum in chloroform solution had three bands in the carbonyl region at 1708  $\text{cm}^{-1}$ , 1760  $\text{cm}^{-1}$ , and 1780  $\text{cm}^{-1}$  attributed to  $\gamma$ -lactam, 5-membered cyclic ketone, and  $\gamma$ -lactone functions respectively.

The alkaline aqueous solution from the chloroform extraction above was acidified with sulphuric acid and extracted with chloroform. The chloroform extracts were dried over anhydrous sodium sulphate and then evaporated to dryness. The residue, 0.030 g. after recrystallization from ether, melted at 205° C.

Calc. for  $\text{C}_{15}\text{H}_{15}\text{O}_5\text{N}$ : C, 61.43; H, 6.48; N, 4.77%. Found: C, 61.40, 61.59; H, 6.63, 6.48; N, 4.85, 5.14%.

The infrared spectrum (nujol) had bands at 1610  $\text{cm}^{-1}$ , 1705  $\text{cm}^{-1}$ , and 1775  $\text{cm}^{-1}$  attributed to amide, carboxylic acid, and  $\gamma$ -lactone functions respectively.

The methyl ester was prepared by treatment of a methanolic solution of the acid with a solution of diazomethane in ether. After several recrystallizations from ether, the ester melted at 122–123° C.

<sup>5</sup>Infrared spectra were determined on a Perkin-Elmer No. 21 recording spectrophotometer.



Calc. for  $C_{16}H_{21}O_5N$ : C, 62.54; H, 6.84; N, 4.56; OMe, 10.08%. Found: C, 62.45, 62.45; H, 7.22, 6.76; N, 4.41, 4.71; OMe, 10.15%.

The infrared spectrum in nujol showed a double peak at 1653 and 1665  $\text{cm}^{-1}$  in the amide region, a peak at 1730  $\text{cm}^{-1}$  assigned to the carbomethoxy group, and a peak at 1788  $\text{cm}^{-1}$  attributed to the  $\gamma$ -lactone function.

#### *Permanganate Oxidation of Annotinine Lactamdiol*

A solution of 0.50 g. of III in 50 ml. of glacial acetic acid was treated with an aqueous solution of potassium permanganate until the pink color was persistent. The excess permanganate was destroyed with methanol and the mixture was evaporated to dryness. The residue suspended in  $H_2O$ , was treated with sulphur dioxide to reduce the manganese dioxide. The acidic solution was then exhaustively extracted with chloroform. The chloroform extracts were worked up as in the procedure above to yield the  $\gamma$ -lactam IV (0.1 g.) and the acid VI (0.1 g.). The aqueous solution from the chloroform extraction was continuously extracted with ether to yield a small sample of the sulphate of amino acid VII identified by its melting point and its infrared spectrum.

#### *Hydrolysis of the Acid $C_{18}H_{19}O_6N$ (VI)*

The procedure followed was that of Woodward and Brehm (14) for the determination of formic acid from N-formyl derivatives. The acid (0.2158 g.) was refluxed for 2 hours with 20 cc. of 2 *N* sulphuric acid. The solution was then distilled and water added to keep the volume approximately constant. The distillate was collected in fractions and titrated with 0.1 *N* sodium hydroxide.

The amount of volatile acid collected corresponded to 0.95 mole per mole of original acid VI. In another run the aqueous distillate gave a positive test for formic acid with mercuric chloride as described in Feigl (2) and also reduced permanganate and bromine.

The aqueous residue after removal of the formic acid was treated alternately with barium hydroxide and sulphuric acid to remove inorganic ions. Evaporation of the solution yielded an amino acid residue which was converted to its methyl ester by diazomethane. The amino acid methyl ester was identical (mixed melting point and infrared spectra) with the methyl ester of amino acid VII prepared from unsaturated lactone A (1).

#### *Reduction of $C_{18}H_{17}O_4N$ (IV) with Sodium Borohydride*

A solution of compound IV (0.100 g.) in 10 ml. of ethanol was added slowly with stirring to a solution of sodium borohydride (0.200 g.) in 10 ml. of ethanol at room temperature. The reaction mixture was stirred for 2 hours before decomposing the excess borohydride first with formaldehyde and then with acetic acid until faintly acid. The solution was then evaporated to dryness under reduced pressure. The residue was dissolved in water, made alkaline with ammonia, and extracted with chloroform. The dried chloroform extracts were evaporated to dryness to yield 0.09 g. of residue which, after three recrystallizations from acetone, melted at 254–255° C.

Calc. for  $C_{18}H_{19}O_4N$ : C, 64.95; H, 6.90%. Found: C, 64.90, 65.19; H, 6.96, 6.86%.

The infrared spectrum in nujol had absorption bands at 3335  $\text{cm}^{-1}$  in the hydroxyl region, at 1682  $\text{cm}^{-1}$  in the  $\gamma$ -lactam region, and at 1781  $\text{cm}^{-1}$  in the lactone region.

#### *Oxidation of Unsaturated Lactone A (VIII) with Barium Permanganate*

Unsaturated lactone A (VIII) was prepared by the procedure outlined by Manske and Marion (8). Incidentally, this procedure proved superior to that described by Meier,



Meister, and Marion (9). The compound VIII (1.86 g.) was dissolved in acetone and treated with aqueous barium permanganate solution until the pink color persisted. The excess permanganate was destroyed by warming with methanol. The manganese dioxide was reduced with sulphur dioxide and the organic solvents steam distilled. The solution was then repeatedly extracted with chloroform. The combined extracts were dried and evaporated to dryness to yield 0.7 g. of residue. Upon addition of acetone a crystalline precipitate separated which, after several recrystallizations from acetone, melted at 205° C. The melting point was not depressed on admixture with the acid  $C_{15}H_{19}O_6N$  (VI) prepared from the lactamdiol. Their infrared spectra were also identical. Total yield: 0.4 g.

The acetone mother liquors from the separation of VI were freed of acetone, taken up in methanol, and treated with a solution of diazomethane in ether. Concentration of the solution yielded a crystalline ester which, after recrystallization from methanol, melted at 193–195° C. with some decomposition. Yield: 0.070 g.

Calc. for  $C_{17}H_{21}O_6N$ : C, 60.89; H, 6.27; N, 4.18; OMe, 9.25%. Found: C, 60.90, 61.00; H, 6.77, 6.74; N, 4.11, 4.30; OMe, 9.09, 9.35%.

The infrared spectrum (nujol) had a double peak at 1633  $cm^{-1}$  and 1645  $cm^{-1}$  in the amide region and single peaks at 1710  $cm^{-1}$ , 1743  $cm^{-1}$ , and 1780  $cm^{-1}$ , corresponding to carbonyl, carbomethoxy, and  $\gamma$ -lactone groups respectively.

Continuous ether extraction of the aqueous solution from the chloroform extraction above yielded the sulphate of the amino acid  $C_{14}H_{19}O_4N$ .

#### *Hydrolysis of the Ester $C_{17}H_{21}O_6N$ (IX)*

The ester IX (0.215 g.) was hydrolyzed with 20 ml. 2 N sulphuric acid by the procedure described previously for the acid VI. The amount of volatile acid collected corresponded to 1 mole per mole of ester used. The aqueous hydrolytic medium was extracted with chloroform to yield a small residue (0.02 g.) which had an infrared spectrum identical with IV. Recrystallization of the residue from ether yielded a few crystals which did not depress the melting point of compound IV.

#### *Ozonolysis of Unsaturated Lactone A (VIII)*

A solution of VIII (0.36 g.) dissolved in 35 ml. of anhydrous ethyl acetate was treated with excess ozone at  $-30^\circ$  (the ozone concentration in the oxygen stream was approximately 3.5% and the time of treatment was 45 minutes). Adams' catalyst (0.025 g.) was added to the cold solution, which was immediately placed under hydrogen pressure (10 p.s.i.g.) for 2 hours. The catalyst was then removed by filtration and the filtrate taken to dryness. The residue was taken up in chloroform, washed with aqueous ammonia, and aqueous hydrochloric acid. Evaporation of the chloroform yielded a residue (0.23 g.) which was dissolved in benzene and adsorbed on alumina. Elution with one volume per cent methanol in benzene yielded 0.18 g. of a compound which melted at 174° C. after recrystallization from ether. This compound proved identical (infrared spectrum and mixed melting point) with the compound  $C_{16}H_{19}O_5N$  prepared by dehydration of hydroxy annotinine lactam by MacLean and Prime (7).

#### *Treatment of Unsaturated Lactone A (VIII) with Cyanogen Bromide*

The lactone VIII was treated with excess cyanogen bromide in anhydrous benzene at room temperature, at 60° C., and at reflux temperature. In each case approximately 80% of the starting material was recovered. The remaining 20% was recovered as a

neutral amorphous precipitate which showed absorption in the infrared at  $1770\text{ cm}^{-1}$  in the lactone region and at  $1650\text{ cm}^{-1}$  unassigned. There was only very slight absorption in the  $\text{N}-\text{C}\equiv\text{N}$  region at  $2200\text{ cm}^{-1}$ . Attempts to purify this compound proved unsuccessful.

#### *Hydrogenolysis of Annotinine over Raney Nickel*

Annotinine (1.4 g.) was dissolved in 75 ml. of methanol containing 0.3 g. Raney nickel and treated with hydrogen at  $150^\circ\text{C}$ . and 2600 p.s.i.g. for a period of 12 hours. The reaction mixture was freed of catalyst, evaporated to dryness, dissolved in chloroform, and adsorbed on a column of alumina. Two products were isolated. The least strongly adsorbed fraction melted at  $108^\circ\text{C}$ ., 0.3 g. (22%), and proved identical with the reduction product of VIII (infrared spectrum and mixed melting point). The second product melted after recrystallization from methanol at  $205^\circ\text{C}$ . Yield: 0.43 g. (31%).

Calc. for  $\text{C}_{16}\text{H}_{23}\text{O}_3\text{N}$ : C, 69.30; H, 8.31; N, 5.0%. Found: C, 69.21, 69.11; H, 8.28, 8.31; N, 4.75, 4.70%.

The infrared absorption spectrum showed bands at  $3515\text{ cm}^{-1}$  in the hydroxyl region and at  $1752\text{ cm}^{-1}$  in the lactone region.

#### *Reduction of Annotinine Lactam in Acid Medium*

Annotinine lactam (0.30 g.) was dissolved in 50 ml. methanol and treated with 0.10 g. of Adams' catalyst and three drops of concentrated hydrochloric acid. The mixture was then shaken with hydrogen for 18 hours at 60 p.s.i.g. The catalyst was removed by filtration and the methanol evaporated to dryness. The residue was taken up in fresh methanol from which there separated 0.1 g. of a white crystalline precipitate which melted at  $275^\circ\text{C}$ . Recrystallization raised the melting point to  $287^\circ\text{C}$ . In admixture with an authentic sample of annotinine lactam chlorohydrin there was no depression in the melting point.

When the mother liquors from the separation of the chlorohydrin above were concentrated almost to dryness and treated with acetone, another compound separated (0.18 g.). After recrystallization from acetone-methanol it melted at  $210-211^\circ\text{C}$ . This material was very soluble in water and methanol, but insoluble in acetone, ether, and chloroform. It gave a Beilstein halogen test and its behavior indicated that it was a salt. The compound proved to be identical with annotinine hydrochloride hemihydrate (6) by melting point and mixed melting point. On basification with ammonia and ether extraction, annotinine was recovered.

#### *Reduction of Annotinine Lactam in Alkaline Medium*

Annotinine lactam (1.0 g.) was dissolved in 100 ml. of methanol, 0.25 g. of Adams' catalyst and a few drops of  $\text{NH}_3$  were added, and the mixture subjected to a hydrogen pressure of 56 p.s.i.g. for 24 hours. The catalyst was removed by filtration and the methanol evaporated to dryness. The white residue was taken up in fresh methanol from which a crystalline material separated which melted at  $298-300^\circ\text{C}$ . alone or in admixture with pure hydroxy annotinine lactam ( $\text{C}_{16}\text{H}_{21}\text{O}_4\text{N}$ ). Further concentration yielded a second crop of impure  $\text{C}_{16}\text{H}_{21}\text{O}_4\text{N}$  melting at  $298^\circ$  but sintering at  $280^\circ\text{C}$ . A third crop of crystals separated which melted from  $210-218^\circ\text{C}$ . Fraction 3 was separated by the use of acetone. The acetone-soluble fraction was recrystallized from methanol to yield slightly impure starting material, m.p.  $218-222^\circ\text{C}$ ., alone or in admixture with pure  $\text{C}_{16}\text{H}_{19}\text{O}_4\text{N}$ . Further recrystallization resulted in the isolation of a pure sample. In all,

0.51 g. of  $C_{16}H_{21}O_4N$  was recovered from the reaction while the residue comprised slightly impure starting material.

#### ACKNOWLEDGMENTS

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## REARRANGEMENT STUDIES WITH C<sup>14</sup>

### III. THE FRIEDEL-CRAFTS ALKYLATION OF ANISOLE WITH 2-PHENYLETHYL-1-C<sup>14</sup> CHLORIDE AND 2-PHENYLETHANOL-1-C<sup>14</sup><sup>1</sup>

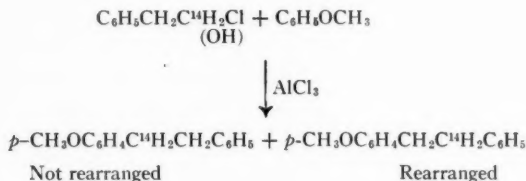
C. C. LEE,<sup>2</sup> A. G. FORMAN,<sup>3</sup> AND A. ROSENTHAL<sup>4</sup>

#### ABSTRACT

The Friedel-Crafts alkylation of anisole with 2-phenylethyl-1-C<sup>14</sup> chloride and 2-phenylethanol-1-C<sup>14</sup> resulted in a product, *p*-methoxydibenzyl, which showed isotope position rearrangement corresponding to an essentially 50% rearrangement of the C<sup>14</sup> labeled atoms from the C-1 to the C-2 positions in the original chloride and alcohol. If one were to assume that both rearrangement and alkylation involve the same intermediate, these results may be explained on the basis of either an ionic mechanism for the Friedel-Crafts alkylation, the rearrangement being attributed to the formation of the phenylethyl cation, or a displacement mechanism in which the alkylation product is formed from a reaction between anisole and a rearranged polarized complex of aluminum chloride and alkylating agent. The possibility that rearrangement in the Friedel-Crafts alkylation may arise from a process separate from and prior to the alkylation stage itself is also discussed. On this basis, the intermediates involved in the rearrangement and alkylation stages will not necessarily have to be the same.

#### INTRODUCTION

The observed rearrangements of alkyl groups in Friedel-Crafts alkylation reactions, such as the formation of isopropylbenzene from the reaction of benzene with *n*-propyl chloride in the presence of aluminum chloride, have served as part of the evidence in support of a mechanism for the Friedel-Crafts alkylation involving ionization of the alkyl halide under influence of the catalyst, followed by an electrophilic substitution on the aromatic nucleus by the carbonium ion (9). Where a rearranged product is found, it may be attributed to a rearrangement of the alkyl carbonium ion, often observed in many S<sub>N</sub>1 type reactions (16). In a recent study using the tracer technique, Roberts, Ropp, and Neville (12) showed that there is no rearrangement in the Friedel-Crafts ethylation of benzene with ethyl-2-C<sup>14</sup> chloride. The observation was interpreted on the basis that the Friedel-Crafts ethylation of benzene may result from either a displacement mechanism, as suggested by Brown and co-workers (1, 6), which would involve no free ethyl fragments, or a carbonium ion mechanism in which the ions reacted with the aromatic nuclei so rapidly as to exclude internal hydride shifts. The present paper deals with another application of the tracer method in the study of rearrangements in the Friedel-Crafts alkylation. The isotope position rearrangement observed in the alkylation of anisole with 2-phenylethyl-1-C<sup>14</sup> chloride and 2-phenylethanol-1-C<sup>14</sup>, as depicted below, is reported.



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## RESULTS AND DISCUSSION

2-Phenylethanol-1-C<sup>14</sup> was prepared by the lithium aluminum hydride reduction of phenylacetic acid-1-C<sup>14</sup>. Conversion of the alcohol to the chloride was effected with thionyl chloride in pyridine (8). That all the C<sup>14</sup> activity was located at the C-1 position was shown by the permanganate oxidation of both the alcohol and the chloride to give nonradioactive benzoic acid.

The alkylation of anisole with either 2-phenylethyl-1-C<sup>14</sup> chloride or 2-phenylethanol-1-C<sup>14</sup> was effected using an excess of anisole as solvent and slightly over one and a half molar equivalents of anhydrous aluminum chloride at 100° C. for several hours. The *p*-methoxydibenzyl obtained was assayed for radioactivity and then oxidized with potassium permanganate to yield anisic acid.

As a check on the total activity, the 2-phenylethyl-1-C<sup>14</sup> chloride was converted to hydrocinnamic acid whose radioactivity was found to be essentially identical with that of the corresponding *p*-methoxydibenzyl. In the alcohol runs, the radioactivity of the phenylurethan of 2-phenylethanol-1-C<sup>14</sup> was also shown to be the same as the corresponding *p*-methoxydibenzyl products.

If there were no rearrangement in the reactions studied, 100% of the total radioactivity in the *p*-methoxydibenzyl should be recovered in the anisic acid. The results from duplicate chloride and alcohol runs are tabulated in Table I, the percentage rearrangement being the difference between 100% and the percentage of total activity actually recovered in the anisic acid.

TABLE I  
REARRANGEMENTS IN THE ALKYLATION OF ANISOLE

Alkylating agent	Compound counted*	Observed activity (c.p.m./sample)†		Corrected activity (c.p.m. on molar basis)‡		% activity in anisic acid		% rearrangement	
		Run I	Run II	Run I	Run II	Run I	Run II	Run I	Run II
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> C <sup>14</sup> H <sub>2</sub> OH	C <sub>6</sub> H <sub>5</sub> NHCOOCH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	590		8850					
	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	594	592	8910	8880				
	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> COOH	567	565	4536	4520	50.9	50.8	49.1	49.2
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> C <sup>14</sup> H <sub>2</sub> Cl	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	1929	1010	17360	9090				
	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	1152	595	17280	8925				
	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> COOH	1073	537	8580	4296	49.7	48.2	50.3	51.8

\*All compounds were converted to barium carbonate and counted as infinitely thick samples of constant geometry in a windowless gas flow counter.

†All samples were counted for a sufficient length of time to ensure statistical deviation of not more than 1-2%.

‡Corrected for the dilution due to non-labeled C atoms. Equals the observed activity multiplied by the number of C atoms per molecule of the compound counted.

These results clearly indicate that essentially 50% rearrangement has taken place in the alkylation of anisole, in the presence of aluminum chloride, by both 2-phenylethyl-1-C<sup>14</sup> chloride and 2-phenylethanol-1-C<sup>14</sup>.\* Although, under our experimental conditions, the yield of alkylation product was only in the order of 10%, results obtained from radioactivity assay of this product are valid. It is, therefore, a fact that 50% rearrangement has taken place at some stage of the reaction process or processes that led to the formation of the isolated alkylation product, *p*-methoxydibenzyl. Such a complete

\*The possibility that the alcohol may undergo prior conversion to the chloride before alkylation is not excluded by the present results.



equilibration of the labeled atoms in the C-1 and C-2 positions of the original chloride and alcohol may best be accounted for by the assumption that the phenylethyl cation is involved, the rearrangement being the result of a 1,2-phenyl shift, or its equivalent, the formation of a phenonium ion (7, 8, 11). These findings, however, do not indicate what exact role such a cation may play in the alkylation step itself in the Friedel-Crafts reaction.

Two possible mechanisms for the Friedel-Crafts alkylation have received considerable current discussion. One of these is an ionic mechanism involving an electrophilic attack on the aromatic ring by a carbonium ion or ion pair (5). The other, believed to be applicable to alkylations with primary halides, postulates a displacement mechanism with the aromatic compound contributing to the breaking of the carbon-halogen bond in the transition state (1, 6). Both of these mechanisms may actually be considered limiting cases of a general process closely related to other types of displacement reactions of alkyl halides (6). In the absence of corroborating kinetic data, isotope position rearrangement alone is not capable of confirming or contradicting mechanisms dealing with the alkylation stage of the Friedel-Crafts reaction. However, if one were to assume that the same intermediate is involved in both rearrangement and alkylation, the present results may be explained on the basis of either an ionic mechanism, the rearrangement being attributed to the formation of the phenylethyl cation, or a displacement mechanism in which the product is formed from a reaction between anisole and a rearranged polarized complex of aluminum chloride and alkylating agent.

The present results may also be accounted for in another way. It is possible that rearrangement observed in the Friedel-Crafts alkylation may arise from a process that is separate from the alkylation stage itself. The finding of Roberts and co-workers (12) that the alkylation of benzene with ethyl-2-C<sup>14</sup> chloride resulted in no rearrangement, while simple contact of the same chloride with aluminum chloride, prior to its use in the alkylation, gave rise to an ethylbenzene with almost 50% rearrangement of the labeled atoms in the ethyl group, appears to indicate that alkylation and rearrangement can be independent of each other. Isotope position rearrangement has also been demonstrated in C<sup>14</sup>-labeled *t*-amyl and *t*-butyl chlorides under the influence of aluminum chloride (10), while the rearrangement of *n*-propyl to isopropyl chloride by contact with aluminum chloride has also been reported (15). Moreover, the work of Hart and others (3, 4) has shown that in the alkylation of phenol with optically active 1-phenylethyl chloride, racemization occurred independently of alkylation, an appreciable part of the observed loss of optical purity being due to racemization prior to alkylation.

On the basis that separate processes account for rearrangement and alkylation in Friedel-Crafts alkylation reactions, the 50% rearrangement observed in the present studies may be visualized as resulting from the action of aluminum chloride on 2-phenylethyl-1-C<sup>14</sup> chloride and 2-phenylethanol-1-C<sup>14</sup>. The aluminum chloride, being a strong Lewis acid, promotes the formation of the labeled phenylethyl cation, affording an opportunity for the 1,2-phenyl shift. The rate of this catalyst-promoted rearrangement must be faster or at least comparable to the rate of alkylation. The phenylethyl system would thus have the opportunity of attaining complete equilibration before yielding the final alkylation product. According to this picture, a rearranged product obtained in a Friedel-Crafts alkylation may be the result of a reaction between the aromatic reactant and a priorly rearranged alkylating agent. The intermediates involved in the rearrangement stage and the alkylation stage do not, therefore, necessarily have to be the same.



If the observed rearrangement in the phenylethylation of anisole were the result of the action of aluminum chloride, effected prior to the alkylation reaction itself, it should be of interest to study whether any rearrangement would take place when 2-phenylethyl-1-C<sup>14</sup> chloride or 2-phenylethanol-1-C<sup>14</sup> is allowed to come into contact with aluminum chloride. However, preliminary trials showed that no 2-phenylethyl chloride could be recovered after this chloride was treated with aluminum chloride for 1 to 2 hours at 100° C., the temperature used in the phenylethylation. With 2-phenylethanol-1-C<sup>14</sup>, some alcohol was recovered after treatment with aluminum chloride at 100° C. for periods of 15 minutes, 2 hours, or 8 hours. Part of the recovered alcohol was converted to the phenylurethan and other portions oxidized to benzoic acid. Radioactivity assays showed rearrangements of only 0.5 to 2.9% as indicated by the activities of the samples of benzoic acid (see Table II). While these results pointed to the fact that the 2-phenyl-

TABLE II  
REARRANGEMENT OF 2-PHENYLETHANOL-1-C<sup>14</sup> AFTER CONTACT WITH ALUMINUM CHLORIDE

Contact time	% alcohol recovered	Corrected activity (c.p.m. on molar basis)		
		Phenylurethan of recovered alcohol	Benzoic acid from recovered alcohol	Per cent rearrangement
15 minutes	38.1	6480±90	35±14	0.5
2 hours	28.6	5505±75	119±14	2.2
8 hours	15.5	5550±75	161±16	2.9

ethanol recovered after contact with aluminum chloride has rearranged only to a small extent, they do not necessarily exclude the possibility that the 50% rearrangement observed in the product of phenylethylation of anisole may be due to a process separate from the alkylation stage. Since the amount of 2-phenylethanol recovered after the aluminum chloride treatment was very small, the Friedel-Crafts alkylation product may be derived from that portion of 2-phenylethanol which was not recoverable after contact with aluminum chloride.

#### EXPERIMENTAL

The preparation of 2-phenylethanol-1-C<sup>14</sup> and 2-phenylethyl-1-C<sup>14</sup> chloride, the oxidation of these compounds to benzoic acid, the conversion of the alcohol to the phenylurethan, and the chloride to hydrocinnamic acid have all been previously reported (7, 8).

##### *Alkylation of Anisole with 2-Phenylethanol-1-C<sup>14</sup>*

Anisole (130 g., 1.20 moles) was placed in a three-necked 250 ml. flask equipped with stirrer, dropping funnel, and condenser. Aluminum chloride (30 g., 0.23 moles) was added and the mixture stirred until solution was effected. 2-Phenylethanol-1-C<sup>14</sup> (17 g., 0.14 moles) was added and the resulting solution, with vigorous stirring, heated on a boiling water bath for 8 hours. The wine-colored solution was then poured into an ice-hydrochloric acid mixture, the organic layer separated, and the aqueous layer extracted with two 100 ml. portions of ether. The combined organic solutions were next washed with five 100 ml. portions of 5% sodium hydroxide and then with dilute hydrochloric acid. It was followed by washing with dilute sodium bicarbonate solution and water. After the mixture had been dried overnight over anhydrous magnesium sulphate,

the solvents were removed and the residue fractionated *in vacuo*. The product was collected over the range 157–163° C. at a pressure of 6 mm. (lit. (14), b.p. at 8 mm., 166–167° C.). On storage for several days in a refrigerator, the liquid product partially solidified. It was then recrystallized three times from 95% methanol. Yields of recrystallized *p*-methoxydibenzyl for the various runs ranged between 2.82 and 2.96 g. (9.7–10.2%), m.p. 60–61° C. (lit. (2, 14), m.p. 61–62° C. and 60–61° C.).

#### *Alkylation of Anisole with 2-Phenylethyl-1-C<sup>14</sup> Chloride*

Anisole (130 g., 1.20 moles) was placed in a three-necked 250 ml. flask equipped with stirrer, dropping funnel, and condenser. Aluminum chloride (30 g., 0.23 moles) was added and the mixture stirred until solution was effected. 2-Phenylethyl-1-C<sup>14</sup> chloride (19.3 g., 0.14 moles) was then introduced and the resulting mixture heated, with continued vigorous stirring, on a boiling water bath for 6 hours. The reaction mixture was hydrolyzed and worked up as described in the alcohol run. Yields of thrice recrystallized *p*-methoxydibenzyl, m.p. 60–61° C., ranged from 9.0 to 9.8%.

#### *Oxidation of p-Methoxydibenzyl*

In a two-necked 1000 ml. flask equipped with condenser and stirrer were placed 500 ml. of 3.2% potassium permanganate solution, 3.5 g. of potassium hydroxide, and 2.0 g. of *p*-methoxydibenzyl. The mixture was refluxed, with stirring, for 120 hours. After the mixture was cooled, the manganese dioxide was filtered off and the colorless filtrate was slowly evaporated to about 200 ml. before it was acidified with dilute sulphuric acid. The resulting solution was repeatedly extracted with ether and the combined extracts dried and then evaporated to dryness. The residue was dissolved in dilute sodium hydroxide, washed with ether, and reacidified. Ether extraction of the acidified solution was repeated, followed by the drying and removal of the ether, and two recrystallizations of the resulting residue yielded pure anisic acid, m.p. 183–184° C. (lit. (13), m.p. 184° C.). Yields for the various runs averaged 0.15 g. (10%).

Considerable amounts of amorphous material may be recovered from the mother liquors after the separation of pure anisic acid. However, attempts to isolate crystalline benzoic acid from this amorphous residue were not successful.

#### *Contact of 2-Phenylethanol-1-C<sup>14</sup> with AlCl<sub>3</sub>*

2-Phenylethanol-1-C<sup>14</sup> (8.4 g., 0.069 moles) was poured onto 15 g. (0.11 moles) of aluminum chloride. A reflux condenser fitted with drying tube was attached and the mixture heated on a boiling water bath. It was then cooled and transferred into an ice-hydrochloric acid mixture, and then repeatedly extracted with ether. The combined extracts were washed with dilute sodium bicarbonate solution and water. After the extracts were dried over anhydrous magnesium sulphate, the ether was removed and the residue distilled at reduced pressure. Half-gram samples of the recovered alcohol were converted to the phenylurethan and to benzoic acid, respectively, by the usual procedures. The weights of alcohol recovered after various lengths of contact time are listed below.

Contact time	Weight of alcohol recovered
15 minutes	3.2 g.
2 hours	2.4 g.
8 hours	1.3 g.

## ACKNOWLEDGMENT

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# THE INFRARED SPECTRA OF $\text{CH}_4$ , $\text{CH}_3\text{D}$ , $\text{CH}_2\text{D}_2$ , $\text{CD}_3\text{H}$ , AND $\text{CD}_4$ <sup>1</sup>

J. K. WILMSHURST<sup>2</sup> AND H. J. BERNSTEIN

## ABSTRACT

The infrared spectra of all the deuterated methanes of high isotopic purity have been obtained with prism resolution and 27 of the 29 fundamentals were observed. The frequencies observed have been compared with the previous grating and prism data and 'best' values of the fundamentals have been suggested. The present data are considered to give more reliable frequencies for most of the fundamentals of  $\text{CH}_3\text{D}$ ,  $\text{CH}_2\text{D}_2$ , and  $\text{CD}_3\text{H}$  than were previously available.

## INTRODUCTION

The infrared spectra of  $\text{CH}_4$  (2, 4, 5, 6, 8, 9, 11, 17, 23),  $\text{CH}_3\text{D}$  (2, 3, 13),  $\text{CH}_2\text{D}_2$  (2, 3),  $\text{CD}_3\text{H}$  (2), and  $\text{CD}_4$  (2, 18, 24) have been studied previously, but since the data for  $\text{CH}_2\text{D}_2$  and  $\text{CD}_3\text{H}$  were obtained only under low resolution, and since new synthetic methods (19) have now made the deuterated methanes available in very high purity, it was considered worth while to reinvestigate all spectra.

The present work was also intended as a survey of the infrared spectra of the methanes preliminary to determining infrared band intensities and bond dipole moments.

## EXPERIMENTAL

$\text{CH}_4$ ,  $\text{CH}_3\text{D}$ ,  $\text{CH}_2\text{D}_2$ ,  $\text{CD}_3\text{H}$ , and  $\text{CD}_4$  were obtained in cylinders of 10 liters at N.T.P. from Merck and Co., Montreal, Canada. The spectra were measured with a Perkin-Elmer model 12-C double pass spectrometer equipped with LiF and NaCl optics and are shown in Figs. 1, 2, 3, 4, and 5 respectively. A 10 cm. gas cell with KBr windows was used in all cases. All the methanes were found by mass spectrographic analysis to be better than 98% pure.

## EXPERIMENTAL RESULTS

A rotational analysis was not performed for  $\text{CH}_4$ ,  $\text{CH}_3\text{D}$ , and  $\text{CD}_4$  since the higher resolution spectra obtained with grating spectrometers have already been analyzed. For  $\text{CH}_2\text{D}_2$  and  $\text{CD}_3\text{H}$  the resolution available here and the overlapping of different bands did not warrant any rotational analysis. Accordingly then, the frequencies recorded are not necessarily for the true band centers but have been taken at the position of maximum intensity in the bands. This approximation to the band center is probably good for parallel bands, which usually have a very sharp  $Q$  branch, but for perpendicular bands, where Coriolis coupling can be quite important, the approximation may be poor.

In Table VII the frequencies of the fundamentals observed in the present investigation are compared with available grating or prism values previously reported and the 'best' value of each fundamental frequency is indicated.

In the following discussion the individual methanes will be treated separately. The numbering of the frequencies is that used by Herzberg (14).

### $\text{CH}_4$

Methane belongs to the point group  $T_d$  and has one totally symmetric and one doubly-degenerate fundamental, both of which are infrared inactive. The two triply-degenerate

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fundamentals,  $\nu_3$  and  $\nu_4$ , are infrared active and have been observed at 3020  $\text{cm}^{-1}$  and 1301  $\text{cm}^{-1}$  respectively in the present investigation. Owing to Coriolis interaction between  $\nu_2(e)$  and  $\nu_4(f_2)$ , the former becomes infrared active and is observed at 1535  $\text{cm}^{-1}$ . The observed spectrum is given in Fig. 1.

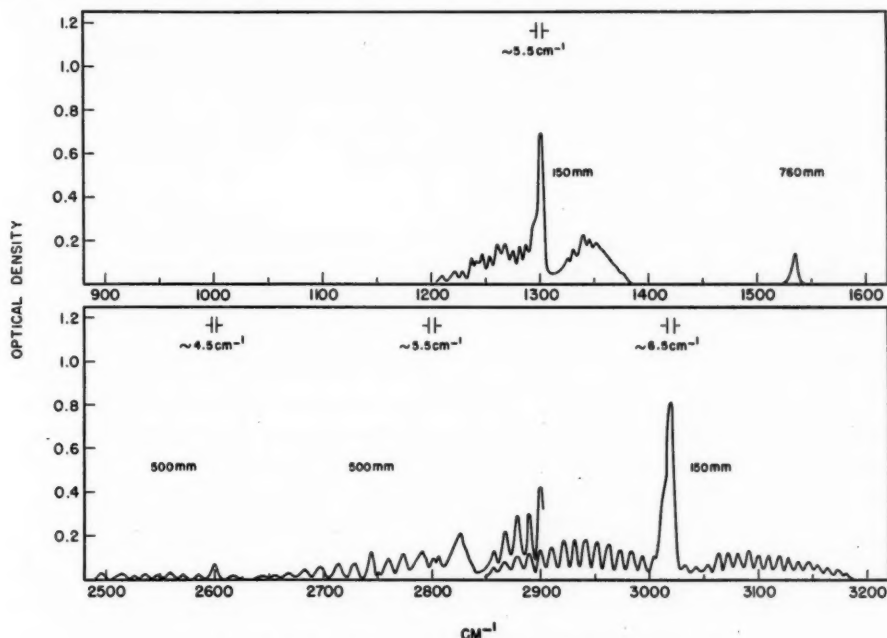


FIG. 1. The infrared spectrum of gaseous  $\text{CH}_4$  in a 10 cm. cell.

The agreement between the fundamentals observed here and the grating values previously reported is good (see Table VII) with the exception of  $\nu_4(f_2)$  which appears to be 5  $\text{cm}^{-1}$  too low, probably owing to the effect of Coriolis coupling in which case the observed position of maximum intensity is not such a good estimate of the band center.

The observed band centers and their assignments are given in Table I.

TABLE I  
OBSERVED INFRARED SPECTRUM OF  $\text{CH}_4$

$\nu$ ( $\text{cm}^{-1}$ )	Assignment
1301	$\nu_4(f_2)$
1535	$\nu_2(e)$
2601	$2\nu_2 = 2602(A_1 + E)$
2826	$\nu_2 + \nu_4 = 2836(F_1 + F_2)$
3020	$\nu_3(f_2)$

### $\text{CH}_3\text{D}$

Monodeuteromethane is a symmetric top belonging to the point group  $C_{3v}$ . The three totally symmetric type  $a_1$  vibrations and three doubly-degenerate type  $e$  modes are all infrared active. The observed spectrum is given in Fig. 2.

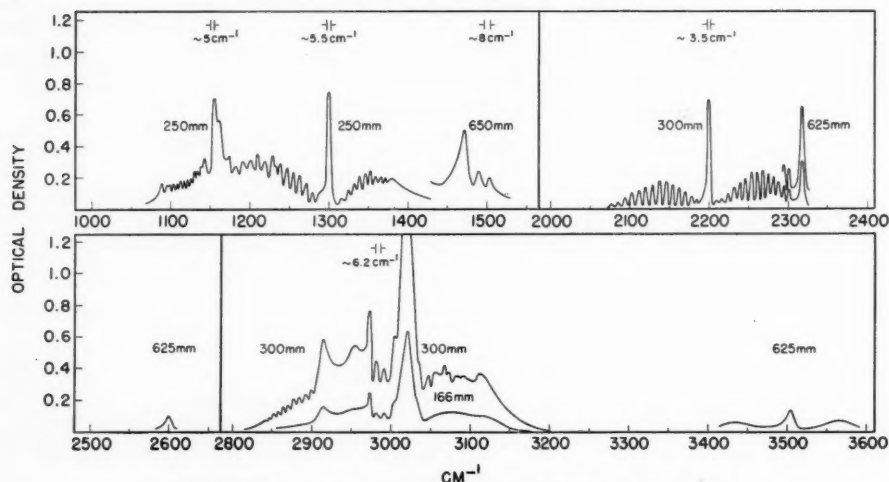


FIG. 2. The infrared spectrum of gaseous  $\text{CH}_3\text{D}$  in a 10 cm. cell.

The rotational constants of  $\text{CH}_3\text{D}$  are calculated (8) as  $A = 5.26 \text{ cm}^{-1}$  and  $B = 3.89 \text{ cm}^{-1}$  with  $r_{\text{CH}} = 1.0925 \text{ \AA}$ . The strong  $Q$  branch at  $2200 \text{ cm}^{-1}$  is assigned as the center of  $\nu_1(a_1)$ , the C—D stretching mode. This band has associated with it  $P$  and  $R$  branches which exhibit rotational spacings of about  $7.7 \text{ cm}^{-1}$  which is consistent with the above  $B$  value. Another parallel type band exhibiting rotational spacings of about  $7.5 \text{ cm}^{-1}$  occurs at  $1300 \text{ cm}^{-1}$  and is assigned to  $\nu_4(a_1)$ , the  $\text{CH}_3$  symmetrical bending mode. The remaining type  $a_1$  vibration  $\nu_{3a}(a_1)$ , arising from the C—H stretching, is not obvious from any of the band structures, but is considered to be associated with the pair of nearly equal maxima at  $2914$  and  $2973 \text{ cm}^{-1}$  owing to Fermi resonance with  $2\nu_2 = 2942 \text{ cm}^{-1}$ . The corresponding unperturbed position of  $\nu_{3a}(a_1)$  is taken as  $2945 \text{ cm}^{-1}$ .

The three prominent maxima at  $3021$ ,  $1471$ , and  $1155 \text{ cm}^{-1}$  are assigned to  $\nu_{3b}(e)$ , the C—H stretching mode;  $\nu_2(e)$ , the  $\text{CH}_3$  bending mode; and  $\nu_{1b}(e)$ , the C—D bending mode, respectively.

The frequencies observed here are for the most part in poor agreement with the grating values determined by Ginsburg and Barker (13), being lower in every case, by  $1 \text{ cm}^{-1}$  at  $1155 \text{ cm}^{-1}$ ,  $7 \text{ cm}^{-1}$  at  $1300$ – $1500 \text{ cm}^{-1}$ ,  $5 \text{ cm}^{-1}$  at  $2200 \text{ cm}^{-1}$ , and  $10 \text{ cm}^{-1}$  at  $2900$ – $3030 \text{ cm}^{-1}$ .

It is felt that the accuracy of the present work is probably superior to that of Ginsburg and Barker, since the recent grating data of Boyd and Thompson (3) give the band center for  $\nu_1$  of  $\text{CH}_3\text{D}$  at  $2200.03 \text{ cm}^{-1}$  in excellent agreement with the value reported here of  $2200 \text{ cm}^{-1}$ , but in poor agreement with Ginsburg and Barker's value of  $2205.25 \text{ cm}^{-1}$ . It would appear desirable in view of the discrepancies reported here to re-examine all of the bands of  $\text{CH}_3\text{D}$  under high resolution in order to obtain more accurate band centers.

The assignment for  $\nu_{3a}(a_1)$  presented here (Table II) differs from that reported in Herzberg (16). In the previous assignment (13) the high frequency component of the doublet at  $2914$  and  $2973 \text{ cm}^{-1}$  was taken as  $\nu_{3a}(a_1)$ , whereas here this doublet is considered to arise from Fermi resonance between  $2\nu_2$  and  $\nu_{3a}$ , giving an unperturbed value of  $\nu_{3a}$  around  $2945 \text{ cm}^{-1}$ . Normal co-ordinate calculations also support this assignment (12, 20, 22).



TABLE II  
 OBSERVED INFRARED SPECTRUM OF CH<sub>3</sub>D

$\nu$ (cm. <sup>-1</sup> )	Assignment
1155	$\nu_{4b}(e)$
1300	$\nu_{4a}(a_1)$
1471	$\nu_2(e)$
2200	$\nu_1(a_1)$
2317	$2\nu_{4b} = 2310(A_1 + E)$
2600	$2\nu_{4a} = 2600(A_1)$
2914 } 2973 }	Fermi resonance between $\nu_{3a}(a_1) = 2945$ and $2\nu_2 = 2942(A_1)$
3021	$\nu_{2b}(e)$
3505	$\nu_1 + \nu_{4a} = 3500(A_1)$

### CH<sub>2</sub>D<sub>2</sub>

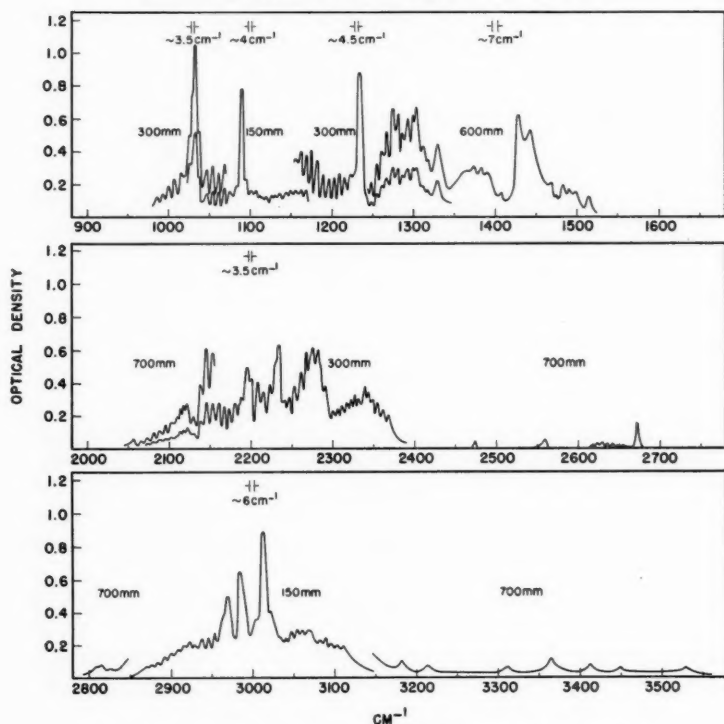
Dideuteromethane belongs to the point group  $C_{2v}$  and has nine nondegenerate vibrations, four of species  $a_1$ , one of  $a_2$ , and two each of  $b_1$  and  $b_2$ . All but the  $a_2$  mode are infrared active. The infrared spectrum is shown in Fig. 3.

The  $b_1$  vibrations give rise to type  $C$  bands and the  $b_2$  to type  $A$  bands. These have pronounced  $Q$  branches. The  $b_1$  and  $b_2$  stretching modes are assigned as 3013 and 2234 cm.<sup>-1</sup> respectively, while the  $b_1$  and  $b_2$  rocking motions occur at 1090 and 1234 cm.<sup>-1</sup> respectively, the 1090 cm.<sup>-1</sup> band being taken, in preference to that at 1033 cm.<sup>-1</sup>, to give agreement with the Teller Redlich product rule. The totally symmetric vibrations will produce type  $B$  bands. From the graphs given by Badger and Zumwalt (1), for band envelopes of  $B$  type bands, the spacing of the doublet  $Q$  branch should be about 13.4 cm.<sup>-1</sup>. Three type  $B$  bands were observed at 2976, 2202, and 1436 cm.<sup>-1</sup>, with doublet spacings of 15, 12, and 12 cm.<sup>-1</sup> respectively. The first of these bands is assigned to  $\nu_{3a}(a_1)$ , the C—H stretching mode, the second to  $\nu_1(a_1)$ , the C—D stretching mode, and the third to  $\nu_{2a}(a_1)$ , the symmetrical bending mode of the CH<sub>2</sub> group. The remaining type  $a_1$  mode corresponding to the symmetrical bending of the CD<sub>2</sub> group did not have a typical type  $B$  structure but was associated with the band at 1033 cm.<sup>-1</sup>. The weak band observed at 1329 cm.<sup>-1</sup>, corresponding to a band at 1333 cm.<sup>-1</sup> in the Raman spectrum (21), is considered to be  $\nu_{2b}(a_2)$  made infrared active by Coriolis coupling. The observed frequencies are given in Table III together with their assignments.

Three bands of CH<sub>2</sub>D<sub>2</sub>, as an impurity in CH<sub>3</sub>D, have previously been observed with a grating instrument by Ginsburg and Barker (13) and again, as in their spectrum of CH<sub>3</sub>D, were higher in frequency than those reported here. Some of the other bands of CH<sub>2</sub>D<sub>2</sub> have been observed in mixtures of the deuterated methanes under low resolution (2) and the agreement with our data is reasonably satisfactory considering the overlapping of the bands in the mixtures. One outstanding point of disagreement occurs in the Raman spectrum (21) where  $\nu_1$  is placed at 2139 cm.<sup>-1</sup>, as compared to the present assignment of 2202 cm.<sup>-1</sup>. Unfortunately no indication of the relative intensity of the Raman bands was reported and it may be that the band at 2180 cm.<sup>-1</sup> assigned to  $2\nu_{4c}$  is actually  $\nu_1$ . However, even here the discrepancy is still large. An investigation of the Raman spectra of all the deuterated methanes is now in progress and it is hoped that this point will be cleared up.

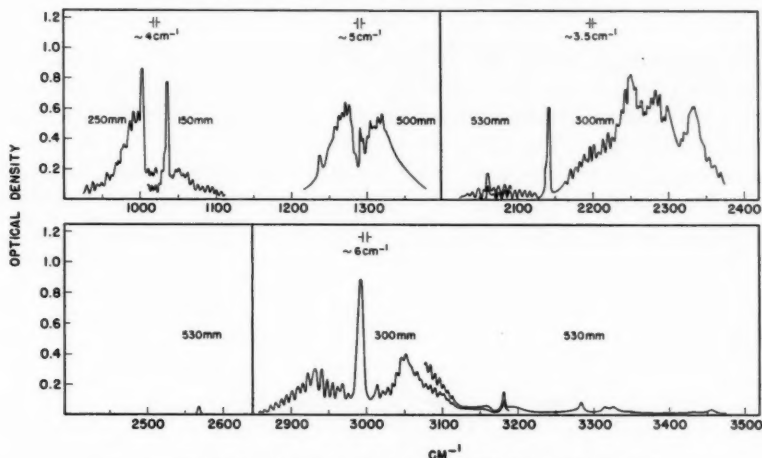
### CD<sub>3</sub>H

Trideuteromethane, like CH<sub>3</sub>D, belongs to the point group  $C_{3v}$ . There are three modes of species  $a_1$  and three of species  $e$ , all six being infrared active. The observed spectrum is given in Fig. 4.

FIG. 3. The infrared spectrum of gaseous  $\text{CH}_2\text{D}_2$  in a 10 cm. cell.TABLE III  
OBSERVED INFRARED SPECTRUM OF  $\text{CH}_2\text{D}_2$ 

$\nu$ ( $\text{cm}^{-1}$ )	Assignment	$\nu$ ( $\text{cm}^{-1}$ )	Assignment
1033	$\nu_{4a}(a_1)$	2672	$\nu_{2a} + \nu_{4c} = 2670(B_1)$
1090	$\nu_{4b}(b_1)$	2816	?
1234	$\nu_{4c}(b_2)$	2969	2976
1329	$\nu_{2b}(a_2)$	2984	
1430	$\nu_{2a}(a_1)$	3013	$\nu_{2b}(b_1)$
1442		3182	$2\nu_{4b} + \nu_{4a} = 3213(A_1)$
2056	$2\nu_{4a} = 2066(A_1)$	3213	$\nu_1 + \nu_{4a} = 3235(A_1)$
~2130	$\nu_{4a} + \nu_{4b} = 2123(B_1)$	3311	$2\nu_{4a} + \nu_{4c} = 3300(B_2)$
2196	$\nu_1(a_1)$	3364	$2\nu_{4b} + \nu_{4c} = 3414(B_2)$
2208		3412	$\nu_1 + \nu_{4c} = 3436(B_2)$
2234	$\nu_{3c}(b_2)$	3449	$\nu_{3c} + \nu_{4c} = 3468(A_1)$
~2275	$\nu_{4a} + \nu_{4c} = 2267(B_2)$	3529	$\{ 2\nu_{4c} + \nu_{4b} = 3558(B_1)$
2474	$\{ \nu_{2a} + \nu_{4a} = 2469(A_1)$		$\nu_{4a} + \nu_{4b} + \nu_{2a} = 3559(B_1)$
2559	$\{ 2\nu_{4c} = 2468(A_1)$		
	$\nu_{2b} + \nu_{4c} = 2563(B_1)$		

The rotational constants (7) for  $\text{CD}_3\text{H}$  are  $A = 2.63 \text{ cm}^{-1}$  and  $B = 3.28 \text{ cm}^{-1}$ . The strong  $Q$  branch at  $2993 \text{ cm}^{-1}$  is assigned as the center of  $\nu_{3a}(a_1)$ , the C—H stretching mode. This band has associated with it  $P$  and  $R$  branches which exhibit rotational spacings of about  $6.5 \text{ cm}^{-1}$ , which is consistent with the above  $B$  value. The strong  $Q$  branch at  $2142 \text{ cm}^{-1}$ , with rotational spacing in the  $P$  branch of about  $6.7 \text{ cm}^{-1}$ , is assigned as

FIG. 4. The infrared spectrum of gaseous  $\text{CD}_3\text{H}$  in a 10 cm. cell.

the center of  $\nu_1(a_1)$ , the C—D stretching mode. The remaining type  $a_1$  frequency  $\nu_{4a}$  is associated with either of the two strong  $Q$  branches at 1036 or 1003  $\text{cm}^{-1}$ . Without a detailed analysis the rotational spacing here is no guide to the assignment, owing to Coriolis coupling between the two modes, but an application of the Teller Redlich ratio rule (15) to  $\text{CH}_3\text{D}$  and  $\text{CD}_3\text{H}$  favors the assignment of the 1003  $\text{cm}^{-1}$  band to  $\nu_{4a}(a_1)$ . The band at 1036  $\text{cm}^{-1}$  is then taken as  $\nu_{4b}(e)$ , the  $\text{CD}_3$  bending mode. The other bending mode,  $\nu_2(e)$ , is assigned to the perpendicular band at 1291  $\text{cm}^{-1}$ .

Assuming the band around 2260  $\text{cm}^{-1}$  to have the same structure as that at 1291  $\text{cm}^{-1}$ , the center is taken at 2263  $\text{cm}^{-1}$  and the band assigned to  $\nu_{3b}(e)$ , a C—D stretching vibration. The observed frequencies and their assignments are given in Table IV.

TABLE IV  
OBSERVED INFRARED SPECTRUM OF  $\text{CD}_3\text{H}$ 

$\nu$ ( $\text{cm}^{-1}$ )	Assignment
1003	$\nu_{4a}(a_1)$
1036	$\nu_{4b}(e)$
1237?	$\nu_{3b} - \nu_{4b} = 1227(A_1 + A_2 + E)$
1291	$\nu_2(e)$
2062	$2\nu_{4b} = 2072(A_1 + E)$
2142	$\nu_1(a_1)$
2263	$\nu_{3b}(e)$
2332	$\nu_2 + \nu_{4b} = 2327(A_1 + A_2 + E)$
2568	$2\nu_2 = 2582(A_1 + E)$
2993	$\nu_{3a}(a_1)$
~3051	$2\nu_{4b} + \nu_{4a} = 3075(A_1 + E)$
3181	$\nu_1 + \nu_{4b} = 3178(E)$
3283	$\nu_{3b} + \nu_{4b} = 3299(A_1 + A_2 + E)$
3315 } 3327 }	$\nu_2 + \nu_{4a} + \nu_{4b} = 3330(A_1 + A_2 + E)$
3456	$\nu_1 + \nu_2 = 3433(E)?$

$\text{CD}_3\text{H}$  has previously been investigated only under low resolution in a mixture of the other deuterated methanes (2), and the reported frequencies agree as well as might be expected with those found here.

$CD_4$ 

Tetradeuteromethane, like  $CH_4$ , belongs to the point group  $T_d$  and has only two infrared active vibrations  $\nu_3(f_2) = 2258 \text{ cm}^{-1}$ , a C—D stretching mode, and  $\nu_4(f_2) = 994 \text{ cm}^{-1}$ , the bending mode. As in  $CH_4$ , the vibration  $\nu_2(e)$  is made active by Coriolis coupling and occurs at  $1098 \text{ cm}^{-1}$ . The spectrum is given in Fig. 5.

The agreement between the frequencies reported here and the band centers obtained from a rotational analysis of the grating data is good for  $\nu_3(f_2)$  where the Coriolis coupling

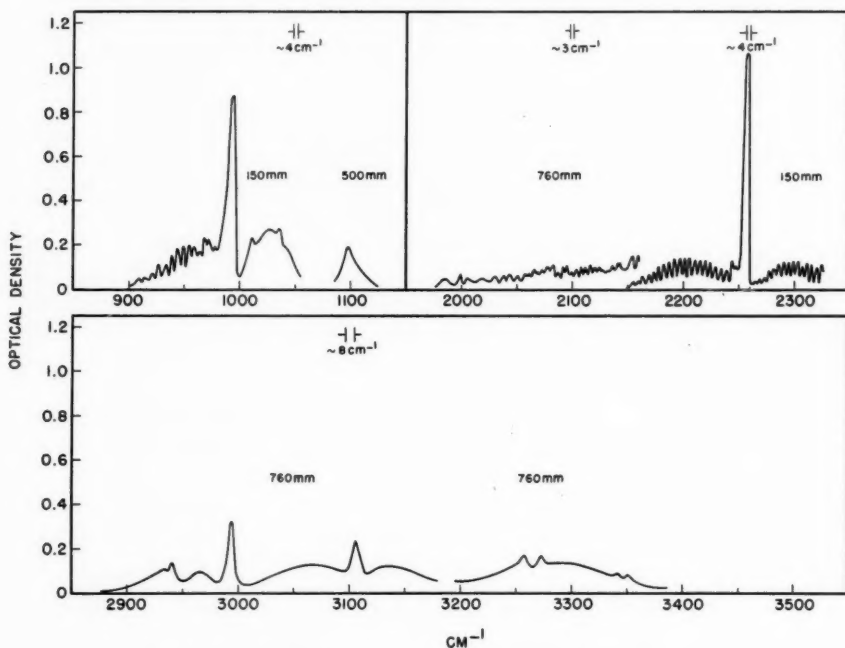


FIG. 5. The infrared spectrum of gaseous  $CD_4$  in a 10 cm. cell.

is very small, but is poorer for  $\nu_2(e)$  and  $\nu_4(f_2)$  where the Coriolis coupling is much larger, the grating values (18) for these two band-centers being  $1092 \text{ cm}^{-1}$  and  $996 \text{ cm}^{-1}$  respectively.

The assignment of the three bands at 2940, 2994, and  $3106 \text{ cm}^{-1}$  is not straightforward, but we suggest the possible assignments  $3\nu_4$  ( $=2982$ ),  $2\nu_4 + \nu_2$  ( $=3086$ ), and  $2\nu_2 + \nu_4$  ( $=3190$ ), the high anharmonicity being in keeping with the triple tones and their relatively high intensities.

Kaylor and Nielsen (18) agree with the first of these assignments, but assume the band at 2994 to be due to  $CD_3H$  as an impurity, while that at  $3106$  is assigned to  $\nu_1 + \nu_4$  ( $=3081$ ). However, the mass spectrometric analysis of our sample indicated that there was only 0.2%  $CD_3H$  present, and it is, therefore, unlikely that this moderately strong band can be explained as an impurity. Again, the assignment of  $3106 \text{ cm}^{-1}$  to  $\nu_1 + \nu_4$  gives a negative anharmonicity and this does not seem likely for a combination tone involving a C—D stretching mode.

TABLE V  
 OBSERVED INFRARED SPECTRUM OF CD<sub>4</sub>

$\nu$ (cm. <sup>-1</sup> )	Assignment
994	$\nu_4(f_2)$
1098	$\nu_2(e)$
~1999	$2\nu_4 = 1988(A_1 + E + F_2)$
2092	$\nu_2 + \nu_4 = 2092(F_1 + F_2)$
2258	$\nu_3(f_2)$
2940	$3\nu_4 = 2982(A_1 + F_1 + 2F_2)$
2994	$2\nu_4 + \nu_2 = 3086(A_1 + E + F_1 + F_2)$
3106	$2\nu_2 + \nu_4 = 3190(F_1 + F_2)$
3258 } 3265	$\nu_3 + \nu_4 = 3252(A_1 + E + F_1 + F_2)$
3272 }	
3341 } 3346	$\nu_2 + \nu_3 = 3356(F_1 + F_2)$
3352 }	

## PRODUCT AND SUM RULES

Application of the product (15) and sum (10) rules to the deuterated methanes is given in Table VI and the agreement between calculated and observed products and sums is satisfactory.

 TABLE VI  
 PRODUCT AND SUM RULES FOR THE DEUTERATED METHANES

		Observed*	Calculated†
$f_2$	$\frac{\nu_3\nu_4(\text{CH}_4)}{\nu_3\nu_4(\text{CD}_4)}$	1.752	1.788
$a_1$	$\frac{\nu_1\nu_3\nu_4(\text{CH}_4)}{\nu_1\nu_3\nu_4(\text{CH}_3\text{D})}$	1.365	1.372
$e$	$\frac{\nu_2\nu_3\nu_4(\text{CH}_4)}{\nu_2\nu_3\nu_4(\text{CH}_3\text{D})}$	1.179	1.180
$a_1$	$\frac{\Pi\nu_{A_1}(\text{CH}_3\text{D})}{\Pi\nu_{A_1}(\text{CD}_3\text{H})}$	1.310	1.337
$e$	$\frac{\Pi\nu_e(\text{CH}_3\text{D})}{\Pi\nu_e(\text{CD}_3\text{H})}$	1.696	1.723
$a_1$	$\frac{\nu_1\nu_2\nu_3\nu_4(\text{CH}_4)}{\nu_1\nu_2\nu_3\nu_4(\text{CH}_2\text{D}_2)}$	1.814	1.885
$a_2$	$\frac{\nu_2(\text{CH}_4)}{\nu_2(\text{CH}_2\text{D}_2)}$	1.147	1.155
$b_1$	$\frac{\nu_3\nu_4(\text{CH}_4)}{\nu_3\nu_4(\text{CH}_2\text{D}_2)}$	1.201	1.206
$b_2$	$\frac{\nu_3\nu_4(\text{CH}_4)}{\nu_3\nu_4(\text{CH}_2\text{D}_2)}$	1.430	1.434

$$\begin{aligned}\Sigma\nu^2(\text{CH}_4) + \Sigma\nu^2(\text{CD}_4) &= 7.068 \times 10^7 \text{ cm.}^{-2} \\ \Sigma\nu^2(\text{CH}_3\text{D}) + \Sigma\nu^2(\text{CD}_3\text{H}) &= 7.073 \times 10^7 \text{ cm.}^{-2} \\ 2 \Sigma\nu^2(\text{CH}_2\text{D}_2) &= 7.076 \times 10^7 \text{ cm.}^{-2}\end{aligned}$$

\* Adopted frequencies were chosen for calculating the ratios and sums.

† Calculated assuming  $\nu_{\text{CH}} = 1.0925$  (see Ref. 15).

## CONCLUSION

It may be seen from the spectra that accurate intensity work can be done on only relatively few bands in the five molecules, viz. (1301+1535) and 3020  $\text{cm}^{-1}$  in  $\text{CH}_4$ ; 2200  $\text{cm}^{-1}$  in  $\text{CH}_3\text{D}$ ; 1291 and 2993 in  $\text{CD}_3\text{H}$ ; (994+1098) and 2258  $\text{cm}^{-1}$  in  $\text{CD}_4$ . Because of this limitation our further interest in the measurement of band intensities has not been pursued.

TABLE VII  
COMPARISON OF THE PRESENT DATA WITH PREVIOUS GRATING OR PRISM DATA

Present investigation		Literature*	Adopted
<b><math>\text{CH}_4</math></b>			
$\nu_1(a_1)$		<b>2915<sup>a</sup></b>	2915
$\nu_2(e)$	1535	1534 <sup>b</sup>	1534
$\nu_3(f_2)$	3020	3019 <sup>c</sup>	3019
$\nu_4(f_2)$	1301	1306 <sup>b</sup>	1306
<b><math>\text{CH}_3\text{D}</math></b>			
$\nu_1(a_1)$	2200	2205 <sup>d</sup>	2200 <sup>e</sup> 2200
$\nu_{3a}(a_1)$	2914 } 2945†	2923 <sup>d</sup>	2945
$\nu_{3b}(a_1)$	2973 }	2983 <sup>d</sup>	
$\nu_{4a}(a_1)$	1300	1307 <sup>d</sup>	1300
$\nu_2(e)$	1471	1477 <sup>d</sup>	1471
$\nu_{3b}(e)$	3021	3031 <sup>d</sup>	3021
$\nu_{4b}(e)$	1155	1156 <sup>d</sup>	1155
<b><math>\text{CH}_2\text{D}_2</math></b>			
$\nu_1(a_1)$	2202	—	2202
$\nu_{2a}(a_1)$	1436	1450 <sup>f</sup>	1436
$\nu_{2b}(a_1)$	2976	2974 <sup>f</sup>	2976
$\nu_{4a}(a_1)$	1033	1036 <sup>d</sup>	1033
$\nu_{2b}(a_2)$	1329	<b>1333<sup>g</sup></b>	1329
$\nu_{3b}(a_1)$	3013	3020 <sup>f</sup>	3013
$\nu_{4b}(b_1)$	1090	1091 <sup>d</sup>	1090
$\nu_{3c}(b_2)$	2234	2255 <sup>f</sup>	2234
$\nu_{4c}(b_2)$	1234	1236 <sup>d</sup>	1234
<b><math>\text{CD}_3\text{H}</math></b>			
$\nu_1(a_1)$	2142	<b>2141<sup>g</sup></b>	2142
$\nu_{3a}(a_1)$	2993	3000 <sup>f</sup>	2993
$\nu_{4a}(a_1)$	1003	—	1003
$\nu_2(e)$	1291	1290 <sup>f</sup>	1291
$\nu_{3b}(e)$	2263	2260 <sup>f</sup>	2263
$\nu_{4b}(e)$	1036	988 <sup>f</sup>	1036
<b><math>\text{CD}_4</math></b>			
$\nu_1(a_1)$	—	<b>2085<sup>g</sup></b>	2085
$\nu_2(e)$	1098	1092 <sup>h</sup>	1092
$\nu_3(f_2)$	2258	2259 <sup>h</sup>	2259
$\nu_4(f_2)$	994	996 <sup>h</sup>	996

\*Grating values in ordinary type, prism values in italics, Raman values in bold type.

†Fermi resonance with  $2\nu_2$ .

<sup>a</sup>See Welsh, H. L., Crawford, M. F., Thomas, T. R., and Love, G. R. *Can. J. Chem.* 30, 577 (1952).

<sup>b</sup>See Reference (5).

<sup>c</sup>See Reference (4).

<sup>d</sup>See Reference (13).

<sup>e</sup>See Reference (3).

<sup>f</sup>See Reference (2).

<sup>g</sup>See Reference (21).

<sup>h</sup>See Reference (18).



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# THE SYNTHESIS AND REACTIONS OF ALKYLATED FURANS<sup>1</sup>

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## ABSTRACT

The reaction of 2-chloromercurifuran with *t*-butyl bromide does not yield 2-*t*-butylfuran. Instead 2,5-di-*t*-butylfuran, 2,2,7,7-tetramethyloctane-3,6-dione, and 2-*t*-butyl-5-[2,4,4-trimethyl-2-pentyl]furan are produced. Air-oxidation of di-*t*-butylfuran yields *trans*-2,2,7,7-tetramethyl-4-octene-3,6-dione (converted to the *cis* isomer photochemically) which forms a dibromide identical with the dibromo substitution product from tetramethyloctanedione. Cold nitric acid oxidation of di-*t*-butylfuran or tetramethyloctanedione yields 4-hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione, but hot nitric acid oxidation of the tetramethyloctanedione yields the expected 2-trimethylacetyl-5-*t*-butylisoxazole. The corresponding oxidation product of *t*-butyltrimethylpentylfuran has not been identified, although it yields 2,2,4,4-tetramethylpentanoic acid, indicative of the iso-octyl substituent, upon hydrolysis. The same acid is obtained by permanganate oxidation of Friedel-Crafts-synthesized 2,5-di-[2,4,4-trimethyl-2-pentyl]furan, a compound which yields *trans*-2,2,4,4,9,9,11,11-octamethyl-6-dodecene-5,8-dione.

Recently alkylfurans have been prepared from furan by Pines and Vesely (13) by use of the boron-trimethyl fluoride-catalyzed reaction with olefins. Earlier Gilman and Wright described the preparation of difurylmethane by reaction of furfuryl chloride with 2-chloromercurifuran (7). At the present time we are reporting the extension of this reaction with chloromercurifuran (I) by use of aliphatic halides.

We have found that *t*-butyl bromide reacts readily with I in chloroform as a medium. The product, however, is not the expected 2-*t*-butylfuran. Instead, 2,5-di-*t*-butylfuran (II), 2,2,7,7-tetramethyloctane-3,6-dione (III), and 2-*t*-butyl-5-[2,4,4-trimethyl-2-pentyl]furan (IV) have been isolated from the reaction mixture in the ratio of about 3 : 1 : 1. The presence of III as a product can be accounted for by the hydrolysis of II while working up the reaction mixture. The yields are low (30% over-all in a typical run). Much resinous material is formed even when the reaction is carried out at reasonably low temperatures (30–40°).

The structures of II and III have been established by the following reactions: When II is treated with bromine water it is converted to 4,5-dibromo-2,2,7,7-tetramethyloctane-3,6-dione (VI). The same product, VI, is formed when III is treated with bromine water. Authentic III was prepared by the method of Wahlberg (19) involving the decarboxylation of 2,2,7,7-tetramethyl-4-carboxy-3,6-octanedione in ether. Kharasch, McBay, and Urry (10) have also described a method for the preparation of III by the action of diacetyl peroxide on pinacolone. Wahlberg (19) has reported a dioxime of III melting at 265°. It is probably an uncorrected value, since in the present investigation the dioxime was found to melt at 277°.

When 2,5-di-*t*-butylfuran (II) is allowed to stand at room temperature over a period of 1 month, it is oxidized, apparently by atmospheric oxygen, to *trans*-2,2,7,7-tetramethyl-4-octene-3,6-dione (V), a pale yellow solid, m.p. 110–111°. The same compound, V, is also formed, along with 4,5-dichloro-2,2,7,7-tetramethyloctane-3,6-dione, when II is treated with acidified hypochlorite solution. Schenck (14, 15, 16, 17, 18) has investigated the autooxidation of furans extensively. In the case of 2,5-dimethylfuran he obtained *trans*-diacetylene, a pale yellow solid, m.p. 77–78°.

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*Trans*-2,2,7,7-tetramethyl-4-octene-3,6-dione (V) is easily converted to the colorless *cis*-modification, m.p. 46°, by exposure to strong sunlight in acetone or hexane solution. Similar observations have been made by Martin, Bett, Romans, and Tidridge (12) in the conversion of *trans*-di-*p*-toluylethylene to the *cis*-isomer by irradiation under mercury vapor light (404.7 mμ). In the case of V, absorption is strong in the region 390–410 mμ, while the *cis*-isomer is relatively transparent over the same range. Of interest, also, is the fact that *trans*-V readily forms a dioxime, m.p. 184°, while *cis*-V fails to react with hydroxylamine. *Trans*-V reacts readily with bromine to form 4,5-dibromo-2,2,7,7-tetramethyloctane-3,6-dione (VI).

The presence of 2-*t*-butyl-5-[2,4,4-trimethyl-2-pentyl]furan (IV) as a product of the reaction between 2-chloromercurifuran (I) and *t*-butyl bromide is surprising but comprehensible. Probably it is formed by an alkylation type of reaction involving two molecules of either *t*-butyl bromide or isobutylene (derived from *t*-butyl bromide) to form diisobutylene (isoöctene), which subsequently alkylates furan.

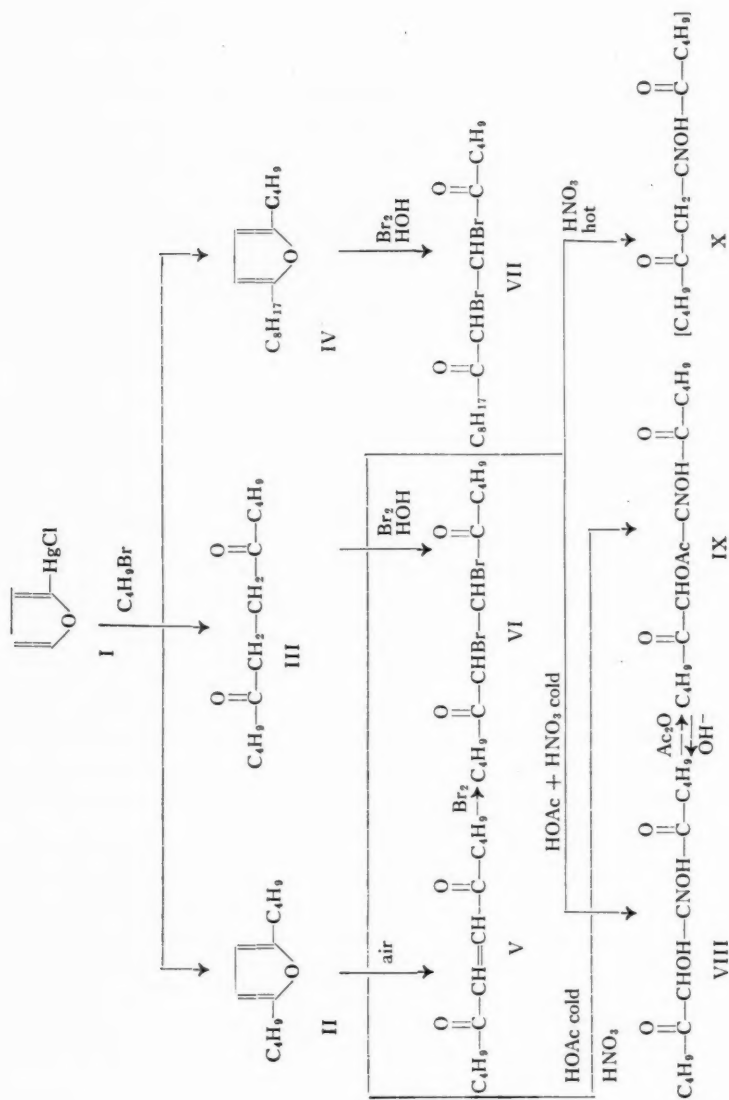
The synthesis of authentic 2-*t*-butyl-5-[2,4,4-trimethyl-2-pentyl]furan (IV) was accomplished by alkylating 2-*t*-butylfuran (prepared by the general method of Pines and Vesely (13)) with diisobutylene. Attempts to prepare IV by the alkylation of 2,4,4-trimethyl-2-pentyl-2-furan with isobutylene failed. When IV is treated with bromine water the product is 4,5-dibromo-2,2,7,7,9,9-hexamethyldecane-3,6-dione (VII).

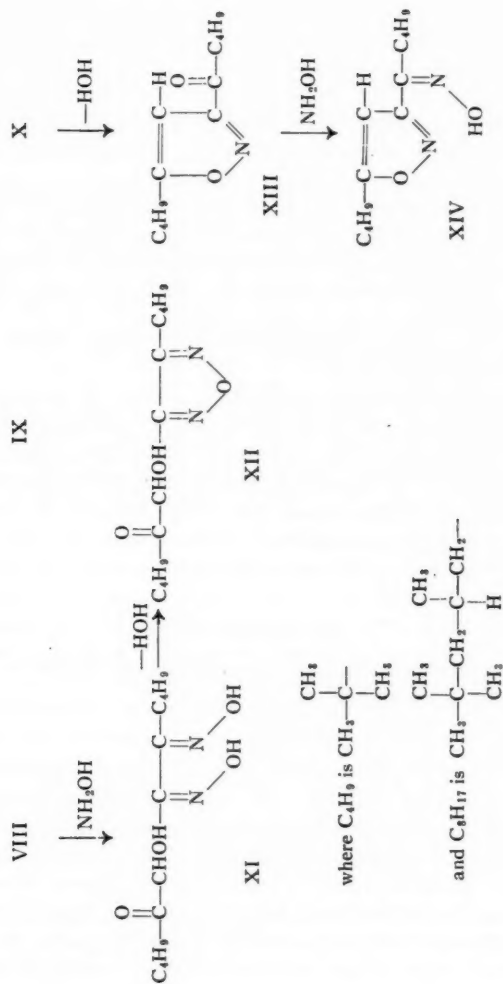
The determination of the molecular weight of VII by the Rast method gave values one-half (206) of that required by theory (412). The same is true for 4,5-dibromo-2,2,7,7-tetramethyloctane-3,6-dione (VI). It has been observed that in both instances decomposition of the bromo compound occurs during the heating period of the molecular weight determination. When the chloro derivative of III (4,5-dichloro-2,2,7,7-tetramethyloctane-3,6-dione) was prepared, values comparable with theory have been obtained for this latter compound.

When [2,4,4-trimethyl-2-pentyl]-2-furan is allowed to stand at room temperature, the original water-white liquid slowly turns yellow and, after 6 weeks, crystals appear. These crystals have been shown to be maleic acid by preparation of the di-*p*-nitrobenzyl ester. Oxidation of 2,4,4-trimethyl-2-pentyl-2-furan with neutral permanganate yields the expected 2,2,4,4-tetramethylpentanoic acid. The authentic acid has been prepared by the method of Whitmore, Wheeler, and Surmatis (20).

During the course of the investigation, 2,5-bis[2,4,4-trimethyl-2-pentyl]furan was also prepared. Unlike 2,5-di-*t*-butylfuran (II), it does not undergo autoxidation readily. However, it is easily oxidized to pale yellow *trans*-2,2,4,4,9,9,11,11-octamethyl-6-dodecene-5,8-dione by the action of dilute nitric acid. A similar reaction has been reported by Lutz and Wilder (11) with compounds such as 2,5-diphenylfuran. In this latter case, however, *cis*-1,2-dibenzoyl-ethylene is formed. When *trans*-octamethyldodecenedione, m.p. 78.5–79.5°, is dissolved in hexane and exposed to strong sunlight, through Pyrex for 12 hours, it is converted to the colorless *cis*-modification, m.p. 55.5–56.5°.

Treatment of 2,5-di-*t*-butylfuran (II) with nitric acid under the conditions employed by Lutz and Wilder (11) yields neither the expected *cis*- nor *trans*-2,2,7,7-tetramethyl-4-octene-3,6-dione (V). Instead, there is obtained 4-hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (VIII) and 4-acetoxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (IX). Treatment of 2,2,7,7-tetramethyloctane-3,6-dione (III) under the same conditions also results in the formation of VIII. When IX is saponified with aqueous sodium hydroxide, VIII is formed. When VIII is treated with acetic anhydride,





IX is the product. The structure for VIII is supported by the fact that it may also be prepared by the addition of nitrous acid to *cis*-2,2,7,7-tetramethyl-4-octene-3,6-dione (V). A similar addition of nitrosyl chloride to *trans*-dibenzoyl ethylene has recently been reported by Beelik and Brown (2).

Alkaline hydrolysis of VIII leads to the formation of ammonia, pivalic acid (trimethylacetic acid), and trimethylpyruvic acid which lends credence to the structure proposed for VIII. Oximation of VIII must occur at the carbonyl function adjacent to the isonitroso function, since the oxime (XI), when steam distilled from alkaline solution, readily loses water and forms the corresponding furazan (XII).

Catalytic hydrogenation of VIII causes the formation of two water-soluble products. In one case, VIII appears to take up 3 moles of hydrogen, while in the other case 1 mole of hydrogen apparently adds. These hydrogenation products have not been investigated further.

When 2,2,7,7-tetramethyloctane-3,6-dione (III) is treated with hot nitric acid, the expected 2-trimethylacetyl-5-*t*-butylisoxazole, XIII, is obtained. Since XIII is a liquid, the oxime, XIV, m.p. 177°, has been prepared, purified, and analyzed. The oxime (XIV) reacts readily with phenylisocyanate and with 2,4-dinitrophenylhydrazine. According to analyses these products seem to be derivatives of XIV rather than of the isomeric 3-*t*-butyl-4-[2-keto-3,3-dimethylbutyl]furazan which might have been expected in consideration of previous work (1, 4).

When 2-*t*-butyl-5-[2,4,4-trimethyl-2-pentyl]furan (IV) is treated with nitric acid (best diluted with acetic acid) a product ( $C_{12}H_{21}NO_3$ ) is produced. This substance, which forms a derivative ( $C_8H_{15}NO_2$ )<sub>n</sub> upon treatment with hydroxylamine, has not of itself been identified. However it is converted under hydrolytic conditions either with acid or alkali to 2,2,4,4-tetramethylpentanoic acid. The presence of the 2,4,4-trimethyl-2-pentyl substituent in IV is thus established.

We are grateful to DuPont of Canada for generous supplies of furan.

#### EXPERIMENTAL

All melting points have been corrected against reliable standards. Molecular weights were determined by the Rast method.

##### *2-t-Butylfuran*

In a three-necked 250-ml. Grignard-type flask, fitted with a stirrer, reflux condenser, and surrounded by an ice-salt bath at -10°, was placed 68 g. (1.0 mole) of furan (DuPont). To the furan, with stirring, was added 2.5 ml. of boron trifluoride etherate (B&A Code 1471) in 2.5 ml. of anhydrous ether. Into this solution was bubbled 56 g. (2.0 mole) of isobutylene (C. P. Matheson) over a period of 75 minutes. Stirring was continued for another 2 hours at 0°. At the end of this time, the contents of the flask had become dark brown. After 125 ml. of water was added to the flask, the mixture was extracted twice with 100-ml. portions of ether, the ether solution washed with saturated aqueous sodium carbonate solution and then dried over anhydrous calcium chloride. The ether was flashed off leaving a brown liquid as a residue. Fractional distillation through a column as described by Bower and Cook (3) yielded two fractions. The first fraction, a colorless liquid, weighed 3.5 g. (2.8%), b.p. 116-117° at 737 mm.;  $n_D^{20}$  1.4373,  $n_D^{25}$  1.4351,  $d_4^{20}$  0.869.



*2,5-Di-*t*-butylfuran (II)**(a) From 2-Chloromercurifuran (I) and *t*-Butyl Bromide*

A slurry of 121.2 g. (0.4 mole) of 2-chloromercurifuran in 220 ml. of chloroform in a three-necked, round-bottom flask fitted with a stirrer was treated with 5 ml. of 95% ethanol and 137.0 g. (1.0 mole) of *t*-butyl bromide. After it was stirred for 7 minutes, the reaction mixture warmed up to the boiling point of chloroform. The heat reaction subsided after 30 minutes and stirring was continued intermittently for 13 days. It was found that the reaction should be allowed to proceed for a minimum of 4 days. Runs worked up after the initial heat reaction had subsided gave negligible yields. At the end of this time, the dark reddish-brown chloroform solution was filtered from the precipitated mercuric halide, extracted 10 times with 100-ml. portions of water, and then with 100 ml. of 5% aqueous sodium hydroxide solution. The chloroform was flashed off leaving a dark brown oil which was distilled under diminished pressure from a Claisen flask. In this manner, 25.5 g. of faintly yellow oil, b.p. 50–105° (10 mm.), was obtained. Three fractions were obtained from this oil. The first fraction weighed 13.3 g. (18.5%); b.p. 49–53° (5 mm.), 210° (760 mm.);  $n_D^{20}$  1.4376;  $d_4^{26.5}$  0.854;  $M_D$  calc., 56.41, found, 56.70. Anal. Calc. for  $C_{12}H_{20}O$ : C, 79.9; H, 11.1. Found: C, 80.1; H, 11.4.

*(b) From 3-Chloromercurifuran and *t*-Butyl Bromide*

When a slurry of 4.9 g. (0.016 mole) of 3-chloromercurifuran, prepared according to the method of Gilman and Wright (7), in 10 ml. of chloroform and 2 ml. of 95% ethanol, was treated with 5.5 g. (0.040 mole) of *t*-butyl bromide the mercurial dissolved and the resulting solution turned reddish-brown over a period of 3 days. After the reaction mixture had been worked up as previously described two oils were obtained by fractional distillation. The first oil weighed 0.56 g. (19%) and boiled at 40–50° at 1–2 mm.

*(c) From Furan and *t*-Butyl Bromide in the Presence of Mercuric Bromide*

When a mixture of 34 g. (0.5 mole) of furan, and 36 g. (0.1 mole) of mercuric bromide in 100 ml. of chloroform, was treated with 24 g. (0.18 mole) of *t*-butyl bromide no apparent reaction occurred after stirring for 10 minutes. However, when 15 ml. of 95% ethanol was added to the mixture, heat was evolved immediately and the reaction mixture began to darken. The heat reaction was sustained by the dropwise addition of a further 113 g. (0.82 mole) of *t*-butyl bromide over a period of 30 minutes. After an additional 20 minutes, the reaction mixture was worked up as described in part (a), and 3.1 g. (3.5%) of 2,5-di-*t*-butylfuran was obtained.

*(d) From Furan and Isobutylene*

A second fraction, a colorless liquid, obtained during the preparation of 2-*t*-butylfuran from furan and isobutylene, weighed 3.6 g. (4.0%); b.p. 61–62° at 16–17 mm.;  $n_D^{20}$  1.4369;  $d_4^{20}$  0.837.

All the oils (a, b, c, and d) were shown to be identical, since on treatment with bromine they all yielded the same product, 4,5-dibromo-2,2,7,7-tetramethyloctane-3,6-dione (VI).

*2-*t*-Butyl-5-[2,4,4-trimethyl-2-pentyl]furan (IV)**(a) From 2-Chloromercurifuran (I) and *t*-Butyl Bromide*

The second fraction, obtained during the preparation of 2,5-di-*t*-butylfuran from 2-chloromercurifuran and *t*-butyl bromide (see (a) above), weighed 4.2 g. (5.4%); b.p.

98–99° at 10 mm.;  $n_D^{20}$  1.4518;  $d_4^{20}$  0.869. Anal. Calc. for  $C_{16}H_{28}O$ : C, 81.3; H, 11.9; mol. wt., 236. Found: C, 81.2; H, 11.5; mol. wt., 248.

(b) *From 3-Chloromercurifuran and t-Butyl Bromide*

The second oil from the distillation described in (b) above weighed 0.40 g. (13%) and boiled at 75–85° at 1–2 mm.

(c) *From Furan and t-Butyl Bromide in the Presence of Mercuric Bromide*

From the reaction mixture obtained by treating furan with *t*-butyl bromide in the presence of mercuric bromide, (c) above, there was obtained 0.9 g. (1.3%) of 2-*t*-butyl-5-isoöctylfuran.

(d) *From 2-t-Butylfuran and Diisobutylene*

In a three-necked 50-ml. Grignard-type flask, fitted with a stirrer, reflux condenser, and cooled externally with tap water (13°), were placed 2.3 g. (0.02 mole) of 2-*t*-butylfuran and 0.5 ml. of boron trifluoride etherate (B&A Code 1471) in 0.5 ml. of anhydrous ether. Diisobutylene, 4.4 g. (0.04 mole), was added dropwise, with stirring, over a period of 20 minutes. After the addition was completed, the reaction mixture was allowed to warm up to room temperature and was stirred for 2 hours. After it had been left for another 16 hours the reaction mixture was poured into 25 ml. of water. Additional ether, 10 ml., was added and the ether phase was washed once with 10 ml. of water, then 10 ml. of saturated aqueous sodium carbonate solution. Finally, the ether solution was dried over anhydrous calcium chloride. After the ether was flashed off, the remaining brown oil was distilled, yielding 3.6 g. (76%) of colorless liquid; b.p. 113–115° at 16–17 mm.;  $n_D^{20}$  1.4522;  $d_4^{20}$  0.839.

All the oils (a, b, c, and d) were shown to be identical, since on treatment with bromine they all yielded the same product, VII.

*2,2,7,7-Tetramethyloctane-3,6-dione (III)*

A third fraction from (a) above weighed 4.5 g. (4.4%); b.p. 106–107° at 10 mm.; m.p. 16.5–18.0°;  $n_D^{20}$  1.4396. Anal. Calc. for  $C_{12}H_{22}O_2$ : C, 72.7; H, 11.2. Found: C, 72.0; H, 11.1.

*2,2,7,7-Tetramethyloctane-3,6-dione Dioxime*

To a solution of 1.0 g. (0.014 mole) of hydroxylamine hydrochloride and 1.0 g. (0.007 mole) of sodium acetate trihydrate in 8 ml. of water was added 0.50 g. (0.0025 mole) of III. This mixture was warmed on the steam bath for 15 minutes, sufficient 95% ethanol being added to dissolve the diketone. A white solid separated. The mixture was cooled, 50 ml. of water added, and the white solid filtered off. The crude product weighed 0.49 g. (99%). It was purified by crystallization from glacial acetic acid yielding 0.10 g. (20%) of white plates; m.p. 277° with decomposition. Anal. Calc. for  $C_{12}H_{24}N_2O_2$ : N, 12.3. Found: N, 12.2.

*2,2,7,7-Tetramethyloctane-3,6-dione Mono-2,4-dinitrophenylhydrazone*

To a solution of 0.08 g. (0.0004 mole) of 2,4-dinitrophenylhydrazine in 0.5 ml. of 93% sulphuric acid and 2 ml. of ethanol was added a solution of 0.10 g. (0.0005 mole) of III in 3 ml. of 95% ethanol. After the solution had been left at room temperature for 30 minutes, orange needles began to form. After 6 hours, 0.12 g. (79%) of orange needles was filtered off. Crystallization from ethanol-water gave 0.08 g. (53%) of fine orange needles, m.p. 122–123°. Further purification was achieved by passing a chloroform solution of the product through a chromatographic column containing alumina (Merck

#71707). This procedure gave a material melting at 129–130°. Anal. Calc. for  $C_{13}H_{26}N_4O_8$ : N, 14.8. Found: N, 14.8.

*2,2,7,7-Tetramethyloctane-3,6-dione Bis-2,4-dinitrophenylhydrazone*

To a solution of 0.36 g. (0.0018 mole) of 2,4-dinitrophenylhydrazine in 1.5 ml. of 93% sulphuric acid and 20 ml. of 95% ethanol was added a solution of 0.20 g. (0.0010 mole) of III in 5 ml. of 95% ethanol. After the solution had been left at room temperature for 20 minutes, yellowish-orange needles began to form. After 1 hour, 0.24 g. (40%) of crude product was filtered off, m.p. 150–165°. Crystallization from 95% ethanol gave 0.10 g. (17%) of orange needles, m.p. 228°. Anal. Calc. for  $C_{24}H_{30}N_8O_8$ : N, 20.1. Found: N, 19.4.

*trans-2,2,7,7-Tetramethyl-4-octene-3,6-dione (V)*

A 7-g. sample of 2,5-di-*t*-butylfuran which had been left for 45 days was observed to have formed a crystalline precipitate. The light yellow solid was filtered off. It weighed 0.08 g. and melted at 105–107°. Crystallization from methanol–water gave 0.05 g. of faintly yellow plates, m.p. 110–111°. Anal. Calc. for  $C_{12}H_{20}O_2$ : C, 73.4; H, 10.3. Found: C, 73.7; H, 10.2.

*trans-2,2,7,7-Tetramethyl-4-octene-3,6-dione Dioxime*

A solution of 0.10 g. (0.0005 mole) of the unsaturated diketone, V, 0.10 g. (0.0014 mole) of hydroxylamine hydrochloride, and 0.10 ml. of pyridine in 1.5 ml. of 95% ethanol was refluxed for 1.5 hours on the steam bath. At the end of this time, the ethanol was removed in a current of air. A white solid precipitated. After 5 ml. of water had been added to the mixture, the solid material was filtered off and washed free from pyridine on the filter. The crude material weighed 0.10 g. and melted at 156–164° with decomposition. Crystallization from ethanol–water gave 0.04 g. (35%) of purified product melting at 184°. Anal. Calc. for  $C_{12}H_{22}N_2O_2$ : C, 63.7; H, 9.80; N, 12.4. Found: C, 63.7; H, 10.1; N, 12.3.

*cis-2,2,7,7-Tetramethyl-4-octene-3,6-dione (V)*

A pale yellow solution of 0.06 g. (0.0003 mole) of *trans*-V in 10 ml. of hexane was placed in a Pyrex flask in bright sunlight for 3 hours. At the end of this time, the solution was colorless. After the hexane was removed in a current of air at room temperature, there remained 0.06 g. (100%) of colorless flat needles, m.p. 44.5–45.0°. Anal. Calc. for  $C_{12}H_{20}O_2$ : C, 73.4; H, 10.3. Found: C, 74.1; H, 10.3.

*4,5-Dibromo-2,2,7,7-Tetramethyloctane-3,6-dione (VI)*

(a) *From 2,5-Di-*t*-butylfuran (II)*

To 50 ml. of saturated bromine water was added 0.5 g. (0.0028 mole) of 2,5-di-*t*-butylfuran. After 2 minutes, a white solid began to form, mixed with the oil. The mixture was allowed to stand for 10 hours, at the end of which time 0.41 g. of crude product was obtained. Crystallization from absolute methanol yielded 0.25 g. (25%) of colorless needles (m.p. 117.5°) with a characteristic sweet odor. Anal. Calc. for  $C_{12}H_{20}Br_2O_2$ : C, 40.5; H, 5.66; Br, 44.9. Found: C, 40.6; H, 5.63; Br, 45.6.

(b) *From 2,2,7,7-Tetramethyloctane-3,6-dione (III)*

In this instance the mixture of bromine water and diketone had to be warmed on the steam bath to promote the reaction. The yield of purified product, m.p. 117.5°, was 4.5%.

(c) From *trans*-2,2,7,7-Tetramethyl-4-octene-3,6-dione (V)

A solution of 0.04 g. (0.0002 mole) of the diketone, V, in 10 ml. of 10% methanol solution of bromine was warmed on the steam bath for 30 minutes, and then allowed to stand overnight at room temperature. Water was then added and a white solid separated. The crude product was purified by crystallization from methanol-water. It weighed 0.04 g. (56%) and melted at 117.5°.

All three products were shown to be identical by mixture melting point.

4,5-Dichloro-2,2,7,7-Tetramethyloctane-3,6-dione

When 3.6 g. (0.02 mole) of 2,5-di-*t*-butylfuran was treated with sodium hypochlorite solution (Javelle water, 7% available chlorine) in excess and the resulting mixture was acidified with hydrochloric acid a pale yellow solid formed in about 3 minutes. Crystallization from methanol gave 0.90 g. (25%) of pale yellow plates, m.p. 110–111°. This compound was shown to be *trans*-III by mixture melting point with an authentic sample.

Further treatment with acidified hypochlorite solution yielded a second solid which, when crystallized from methanol (11.3 ml./g.), gave 1.43 g. (27%) of coarse white needles, m.p. 125–126°. Anal. Calc. for  $C_{12}H_{20}Cl_2O_2$ : Cl, 26.6; mol. wt., 267. Found: Cl, 26.9; mol. wt., 282.

6,7-Dibromo-2,2,4,4,9,9-hexamethyldecane-5,8-dione (VII)

When 0.5 g. (0.002 mole) of 2-*t*-butyl-5-[2,4,4-trimethyl-2-pentyl]furan, IV, was treated with excess bromine water over a period of 6 days, 0.02 g. (23%) of white needles formed. Crystallization from isopropyl alcohol-water gave 0.010 g. (12%) of white needles, m.p. 80–81°. Anal. Calc. for  $C_{16}H_{28}Br_2O_2$ : C, 46.6; H, 6.84; Br, 38.8. Found: C, 47.0; H, 6.86, Br, 39.0.

2-Chloromercuri-5-*t*-butylfuran

A solution of 0.50 g. (0.0040 mole) of 2-*t*-butylfuran in 5 ml. of 95% ethanol was added to 24 ml. of mercurating solution as described by Gilman and Wright (7). After the mixture had been left at room temperature with occasional shaking for 48 hours, the resulting light brown solid, 0.52 g., was removed by filtration. Crystallization from ethanol-water gave 0.33 g. (23%) of white stubby needles, m.p. 164–165°. A mixture melting point of the substance with 2-chloromercuri-5-*t*-butylfuran, m.p. 164–165°, prepared according to the method of Gilman and Wright (7) and Gilman and Calloway (6) showed no depression. Gilman and Burtner (5) report the melting point as 174–175°. Although these mercurials were adequate for derivative identification, it seems evident that one of these two reactions must give an abnormal product. Anal. Calc. for  $C_8H_{11}ClHgO$ : C, 26.7; H, 3.09. Found: C, 26.4; H, 3.10.

[2,4,4-Trimethyl-2-pentyl]-2-furan

In a 500-ml. three-necked round-bottom flask, fitted with a stirrer, reflux condenser, and cooled externally with tap water (12°), was placed 136 g. (2.00 mole) of furan (DuPont). Addition of 5 ml. of boron trifluoride etherate (B&A Code 1471) in 5 ml. of anhydrous ether over a period of 15 minutes caused the formation of a small amount of brown insoluble substance. To this mixture was added 112 g. (1.00 mole) of diisobutylene (Shell Oil Co.) over a period of 25 minutes. Stirring was continued for another 2 hours at 12° and then for an additional 17 hours at 25°. The dark brown mixture was washed three times with 75-ml. portions of water and twice with 50-ml. portions of saturated aqueous sodium carbonate solution, followed by a further two washings

with 75-ml. portions of water. After filtering, a brown liquid, which fluoresced green, was obtained. It was dried over anhydrous calcium chloride. Fractional distillation yielded two products. The first fraction, a colorless liquid, weighed 32 g. (18%) and had b.p. 72–73° at 12–13 mm.;  $n_D^{20}$  1.4567;  $d_4^{20}$  0.877. Anal. Calc. for  $C_{12}H_{20}O$ : C, 79.9; H, 11.1. Found: C, 80.2; H, 11.2.

*2,5-Di-[2,4,4-trimethyl-2-pentyl]furan*

A second fraction, a very pale yellow oil, from the preceding distillation, weighed 21 g. (14%). It had b.p. 113–144° at 1–2 mm.;  $n_D^{20}$  1.4651;  $d_4^{20}$  0.866. Anal. Calc. for  $C_{20}H_{36}O$ : C, 82.1; H, 12.4. Found: C, 82.1; H, 12.2.

*Oxidation of [2,4,4-Trimethyl-2-pentyl]-2-furan*

(a) *Autoxidation to Yield Maleic Acid*

When pure trimethylpentylfuran was allowed to stand at room temperature, the original colorless liquid took on a yellow color over a period of 6 weeks and colorless crystals (needles) began to deposit. These crystals, after being washed with hexane, had m.p. 141–142°. They were identified as maleic acid both by mixture melting point with authentic maleic acid, prepared by the method of Hurd, Roe, and Williams (9), and also by mixture melting point of the di-*p*-nitrobenzyl ester with authentic di-*p*-nitrobenzyl ester of maleic acid. No success attended our efforts to isolate a second moiety as the result of the autoxidation of the trimethylpentylfuran.

(b) *Permanganate Oxidation to Yield 2,2,4,4-Tetramethylpentanoic Acid*

When 9.0 g. (0.05 mole) of [2,4,4-trimethyl-2-pentyl]-2-furan and 200 ml. of water were placed in a 1-liter, three-necked flask equipped with stirrer and reflux condenser and finely ground potassium permanganate was added over a period of 2 days, 23.8 g. (0.15 mole) of the latter was consumed. During the addition period the flask was heated on a steam bath. After the manganese dioxide had been filtered off, the clear colorless filtrate was acidified with hydrochloric acid whereupon an oil separated. The oil failed to crystallize after chilling to 5° and seeding with authentic 2,2,4,4-tetramethylpentanoic acid prepared by the method of Whitmore, Wheeler, and Surmatis (20). The mixture was extracted with ether (3 times with 75 ml. portions) and the ether solution dried over anhydrous sodium sulphate. After the ether was flashed off there remained 3.5 g. (43%) of a colorless oil. Distillation gave 2.3 g. (29%) of colorless oil, b.p. 82° at 2–3 mm. Preparation of the amide by a conventional method gave thin plates, m.p. 68.0–69.5°. A mixture melting point of the amide with authentic amide of tetramethylpentanoic acid showed no depression.

*trans-2,2,4,4,9,9,11,11-Octamethyl-6-dodecene-5,8-dione*

When 2.9 g. (0.01 mole) of 2,5-di-[2,4,4-trimethyl-2-pentyl]furan was treated with 20 ml. of 35% nitric acid solution at room temperature a yellow solid formed over a period of 8 days. The crude material weighed 1.7 g. When it was crystallized from 90% methanol (13 ml./g.) 1.3 g. (42%) of pale yellow needles, m.p. 78.5–79.5°, was obtained. Anal. Calc. for  $C_{20}H_{36}O_2$ : C, 77.8; H, 11.8. Found: C, 77.8; H, 11.9.

*cis-2,2,4,4,9,9,11,11-Octamethyl-6-dodecene-5,8-dione*

A pale yellow solution of 0.20 g. (0.0006 mole) of the *trans*-isomer in 2 ml. of hexane was irradiated with sunlight through Pyrex for 12 hours over a period of 2 days. When the hexane was removed under diminished pressure there remained 0.20 g. (100%) of white solid, m.p. 53–54°. Crystallization from methanol gave 0.16 g. (80%) of white



crystals, m.p. 55.5–56.5°. Anal. Calc. for  $C_{20}H_{36}O_2$ : C, 77.8; H, 11.8. Found: C, 77.8; H, 11.9.

*4-Hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (VIII)*

*(a) From 2,2,7,7-Tetramethyloctane-3,6 dione (III) and Nitric Acid*

When 0.25 g. (0.0013 mole) of III was treated with 6 ml. of 35% nitric acid a precipitate formed within 15 minutes. After the solution had been left for 2 days, 0.38 g. of crude white solid was filtered off. Crystallization from hexane gave 0.14 g. (46%) of white needles, m.p. 162°. Anal. Calc. for  $C_{12}H_{21}NO_4$ : C, 59.2; H, 8.70; N, 5.75. Found: C, 59.4; H, 8.55; N, 5.35.

*(b) From 2,5-Di-*t*-butylfuran (II) and Nitrous Acid*

To an aqueous solution of nitrous acid, prepared by dissolving 0.5 g. of sodium nitrite in 4 ml. of water and adding excess hydrochloric acid, was added 0.25 g. (0.0014 mole) of 2,5-di-*t*-butylfuran. After the solution was left for 30 minutes a crystalline substance formed. It weighed 0.13 g. Crystallization from petroleum ether (60–70°) gave 0.03 g. (90%) of white needles melting at 162°. The product was identical with that obtained by the action of nitric acid on III.

*(c) From cis-2,2,7,7-Tetramethyl-4-octene-3,6-dione (V) and Nitrous Acid*

A solution of 0.010 g. (0.00005 mole) of *cis*-V in 1 ml. of dioxane and 1 ml. of water was treated with 0.2 g. (0.003 mole) of sodium nitrite and 0.5 ml. of glacial acetic acid. The mixture was allowed to stand for 12 hours. At the end of this time, 4 ml. of water was added. A white solid separated. Crystallization from hexane gave 0.005 g. (41%) of white needles, m.p. 162°.

*(d) From 4-Acetoxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (IX)*

A solution of 0.10 g. (0.00035 mole), of IX in 1 ml. of 5% aqueous sodium hydroxide was prepared by adding the sodium hydroxide solution dropwise to the solid material. In 4 minutes, solution was complete. The solution was slightly yellow in color. After 5 minutes a precipitate appeared. On the addition of 3 ml. of water the precipitate did not dissolve. The solution had a pH of 11 (Hydron Paper). The precipitate was filtered off, washed with water, and dried by suction. It weighed 0.05 g. (59%) and melted at 160–161°. A mixture melting point with authentic VIII was not depressed.

*(e) From 2,5-Di-*t*-butylfuran (II) and Nitric Acid*

A solution of 5.0 g. (0.028 mole) of 2,5-di-*t*-butylfuran in 30 ml. of glacial acetic acid was added slowly to a rapidly stirred solution of 5 ml. of 70% nitric acid in 10 ml. of glacial acetic acid. Heat was evolved and a temperature of 25–30° was maintained throughout the reaction time by means of a water bath. Oxides of nitrogen were evolved during the addition. After 45 minutes a heavy white crystalline precipitate formed and the liquid became lime-green in color. The white solid was filtered off, washed with glacial acetic acid, and dried by suction on the filter. The washings were added to the filtrate, which was set aside to check for further precipitation. The product weighed 1.05 g. (15%) and melted at 162°. Crystallization from ethanol–water, methanol–water, and petroleum ether did not raise the melting point. No further precipitation occurred in the filtrate. After the addition of 150 ml. of water a gummy precipitate, weighing 4.0 g., was obtained. The filtrate from this operation was shown to contain trimethylpyruvic acid. The phenylhydrazone of this acid was prepared according to the procedure of Glucksmann (8), who reported the melting point as 157–158°. We found the melting point to be 166.5°. Anal. Calc. for  $C_{12}H_{16}N_2O_2$ : N, 12.7. Found: N, 12.6.



Fractional crystallization of the 4.0 g. of crude gummy solid from petroleum ether (60–64°) yielded 0.6 g. (9%) of white needles, m.p. 162°, which were shown to be VIII for an over-all yield of 24%.

*4-Acetoxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (IX)*

(a) *From 2,5-Di-*t*-butylfuran (II), Nitric Acid, and Glacial Acetic Acid*

From the preceding fractional crystallization, there was also isolated 0.5 g. (6%) of coarse white crystals, m.p. 104–105°. Anal. Calc. for  $C_{14}H_{23}NO_5$ : C, 58.9; H, 8.18; N, 4.91. Found: C, 59.0; H, 8.12; N, 4.92.

(b) *From 4-Hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (VIII)*

When 0.12 g. (0.0005 mole) of VIII was warmed on the steam bath with 5 ml. of acetic anhydride for 5.5 hours, a pale yellow solution resulted. Addition of 50 ml. of water to this solution caused the separation of a colorless oil which crystallized on standing for 15 hours at room temperature. It weighed 0.05 g. (35%) and melted at 96–103°. Crystallization from hexane gave coarse white needles, m.p. 105°. A mixture melting point with the product obtained in (a) above showed no depression.

*4-Hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione Monoxime (XI)*

To a solution of 1.0 g. (0.014 mole) of hydroxylamine hydrochloride and 1.0 ml. (0.013 mole) of pyridine in 10 ml. of 95% ethanol was added 0.58 g. (0.0024 mole) of VIII. The resulting solution was refluxed for 2 hours, then the ethanol removed in a current of air and 15 ml. of water added. The resulting white solid was filtered off and dried by suction. The crude product weighed 0.67 g. and melted at 172°. Crystallization from benzene gave 0.40 g. (65%) of white plates melting at 193–194° with decomposition. Anal. Calc. for  $C_{12}H_{22}O_4N_2$ : C, 55.8; H, 8.59; N, 10.8. Found: C, 55.9; H, 8.36; N, 10.6.

*4-Hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione Mono-2,4-dinitrophenylhydrazone*

To a solution of 0.16 g. (0.0008 mole) of 2,4-dinitrophenylhydrazine in 1 ml. of 93% sulphuric acid and 3 ml. of 95% ethanol was added a solution of 0.243 g. (0.001 mole) of VIII in 7 ml. of 95% ethanol. The resulting solution was allowed to stand at room temperature for 18 hours. At the end of this time, 75 ml. of water was added to the reaction mixture causing the precipitation of 0.34 g. (100%) of a yellowish-orange solid, m.p. 180–185°. Crystallization from ethanol–water gave 0.22 g. (65%) of coarse orange needles, m.p. 210–211°. Anal. Calc. for  $C_{18}H_{26}N_6O_7$ : N, 16.6. Found: N, 16.3.

*3-*t*-Butyl-4-[2-keto-1-hydroxy-3,3-dimethylbutyl]furazan (XII)*

To 5 ml. of 5% aqueous sodium hydroxide solution was added 0.24 g. (0.0009 mole) of XI. The solid dissolved readily and in 2 minutes the solution began to turn yellow. The solution was immediately steam distilled and a colorless oil obtained as a distillate. This oil, on standing, crystallized to a white solid which weighed 0.03 g. (14%) and melted at 62°. Crystallization from methanol–water did not raise the melting point. Anal. Calc. for  $C_{12}H_{20}N_2O_3$ : C, 60.0; H, 8.39; N, 11.7. Found: C, 60.0; H, 8.43; N, 11.3.

The alkaline residue from the steam distillation above yielded a phenylhydrazone which was identified as the phenylhydrazone of trimethylpyruvic acid by mixture melting point with an authentic sample, m.p. 166.5°. This melting point (water–ethanol crystallization) is higher than that (157–158°) previously reported (8).

*2,4-Dinitrophenylhydrazone of 3-t-Butyl-4-[2-keto-1-hydroxy-3,3-dimethylbutyl]furan*

To a solution of 0.034 g. (0.00017 mole) of 2,4-dinitrophenylhydrazine, in 0.25 ml. of 93% sulphuric acid and 1 ml. of 95% ethanol, was added a solution of 0.05 g. (0.0002 mole) of XII in 2 ml. of 95% ethanol. After the solution was left at room temperature for 6 hours, an orange-colored crystalline solid began to separate. Seven days later 0.07 g. (98%) of orange prisms, m.p. 264–266°, was filtered off. Crystallization from glacial acetic acid gave 0.03 g. (42%) of pure product, m.p. 270–271°, with decomposition. Anal. Calc. for  $C_{13}H_{24}N_6O_6$ : N, 20.0. Found: N, 20.1.

*2,4-Dinitrophenylhydrazone of Trimethylpyruvic Acid*

Trimethylpyruvic acid was prepared according to the method of Glucksmann (8). Treatment of an aqueous solution of the acid with an excess of a saturated solution of 2,4-dinitrophenylhydrazine in 2% hydrochloric acid solution readily gave the 2,4-dinitrophenylhydrazone in the form of long canary-yellow needles. When purified by crystallization from ethanol–water it melts at 176.0–176.5°. Anal. Calc. for  $C_{12}H_{14}N_4O_6$ : N, 18.1. Found: N, 17.5.

*Alkaline Hydrolysis of 4-Hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (VIII) to Yield Pivalic Acid (Trimethylacetic Acid) and Trimethylpyruvic Acid*

A solution of 1.0 g. (0.004 mole) of VIII in 20 ml. of 5% aqueous sodium hydroxide turned yellow when warmed and ammonia was given off. The solution was acidified with sulphuric acid and steam distilled. A colorless oil was obtained as a product, mixed with water. The mixture was extracted with ether and the ether extract dried over Drierite. After the ether was evaporated, 0.49 g. of faintly yellow liquid remained. A 0.1 g. portion of this liquid was dissolved in 2 ml. of ether and treated with excess ammonia solution. When the solution was evaporated to dryness a white crystalline substance melting at 132° was obtained. Sublimation under diminished pressure (15 mm. Hg) gave a pure product melting at 138°. A mixture melting point with ammonium pivalate (ammonium trimethylacetate) showed no depression.

In another experiment 0.13 g. (0.005 mole) of VIII was dissolved in 5 ml. of 5% aqueous sodium hydroxide and warmed on the steam bath for 1 hour. At the end of this time, the solution was acidified with hydrochloric acid and treated with an excess of a saturated solution of 2,4-dinitrophenylhydrazine in 2% hydrochloric acid solution. A canary-yellow precipitate formed. On crystallization from ethanol–water this substance gave canary-yellow needles melting at 176.0–176.5°. A mixture melting point with the 2,4-dinitrophenylhydrazone of trimethylpyruvic acid showed no depression.

*3-Trimethylacetyl-5-t-butylisoxazole (XIII)*

When 2.7 g. (0.013 mole) of 2,2,7,7-tetramethyloctane-3,6-dione (III) in 40 ml. of glacial acetic acid was treated with 5 ml. of nitric acid (70%; sp. gr. 1.42) and warmed on the steam bath for 2 hours, oxides of nitrogen were evolved. After the darkening solution had been concentrated to a volume of 20 ml. it was made alkaline by the addition of 10% sodium carbonate solution. A red oil separated which was taken up in ether and dried over anhydrous sodium sulphate. After the ether was flashed off there remained 2.7 g. (99%) of a reddish-brown oil. Distillation gave 1.5 g. (55%) of orange-colored oil, b.p. 90–100° at 2 mm. The compound was converted to its oxime for analysis.

*3-Trimethylacetyl-5-t-butylisoxazole Oxime (XIV)*

A solution of 1.0 g. (0.0048 mole) of 3-trimethylacetyl-5-t-butylisoxazole (XIII) in 10 ml. of absolute ethanol was treated with 1.39 g. (0.02 mole) of hydroxylamine hydro-

chloride and 1.58 g. (0.02 mole) of pyridine. The mixture was refluxed for 2 hours at the end of which time the alcohol was removed in a current of air. After the addition of water to the mixture, a yellow gummy mass formed. The material was taken into solution in hot hexane and on cooling 0.10 g. of white needles, m.p. 168–170°, with decomposition, was obtained. A second crop weighed 0.22 g., m.p. 146–155. The total yield of crude product was 31%. Subsequent crystallization from hexane and ethanol-water gave 0.10 g. (9.3%) of white needles, m.p. 177° (decomposition with gas formation). Anal. Calc. for  $C_{12}H_{20}N_2O_2$ : C, 64.2; H, 8.99; N, 12.5; mol. wt., 224. Found: C, 64.1; H, 9.08; N, 12.2; mol. wt., 213.

When 3-trimethylacetyl-5-*t*-butylisoxazole oxime (XIV) was treated with 2,4-dinitrophenylhydrazine, a yellow product, which melted at 184°, was obtained. According to analysis this may be 3-trimethylacetyl-5-*t*-butylisoxazole dinitrophenylhydrazone. Anal. Calc. for  $C_{18}H_{23}N_5O_5$ : C, 55.5; H, 5.95; N, 18.0. Found: C, 55.5; H, 6.03; N, 18.4.

When 0.10 g. (0.00045 mole) of the isoxazole oxime, XIV, in 2.5 ml. of absolute ether was treated with 0.07 g. (0.0006 mole) of phenylisocyanate for 12 days some N,N'-diphenylurea had precipitated. Decantation of the ethereal supernatant layer followed by evaporation left 0.16 g. of white solid which was crystallized from hexane, 0.11 g. (71%), m.p. 121.5–122.5°. This product may be N-[5-*t*-butylisoxazol-3-methanoyl]-N-*t*-butyl-N'-phenylurea. Further crystallization of this substance from ethanol-water gave 0.075 g. (49%), m.p. 123.0–123.8°. Anal. Calc. for  $C_{19}H_{26}N_4O_3$ : C, 66.4; H, 7.34. Found: C, 67.0; H, 7.38.

*Catalytic Hydrogenation of 4-Hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (VIII)*

When 1.0 g. (0.004 mole) of VIII in 50 ml. of absolute ethanol was hydrogenated for 44 hours at 50 p.s.i.g., using a total of 0.3 g. of platinum oxide catalyst in 0.1 g. portions, 13 lb. (pressure) of hydrogen was absorbed. (A Parr low-pressure hydrogenation apparatus was used.) The drop in pressure corresponded to 0.013 mole of hydrogen or 3 moles of hydrogen per mole of 4-hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (VIII). When the ethanol was removed under diminished pressure there remained 0.94 g. of a thick yellow oil which slowly changed to a gummy solid. Fractional crystallization from water yielded two products.

The first product, clusters of flat rectangles, weighed 0.17 g. (17%), m.p. 136°. Anal. Calc. for  $C_{12}H_{27}NO_4$ : C, 57.8; H, 10.9; N, 5.62. Found: C, 57.9; H, 10.9; N, 5.66.

The second product, which crystallized in the form of fine white needles, weighed 0.02 g. (1.9%) and melted at 150°. Anal. Calc. for  $C_{12}H_{23}NO_4$ : C, 58.8; H, 9.45; N, 5.71. Found: C, 58.7; H, 9.58; N, 6.34.

*Action of Nitric Acid on 2-*t*-Butyl-5-[2,4,4-trimethyl-2-pentyl]furan (IV) to Form  $C_{12}H_{21}NO_3$*

A solution of 2.3 g. (0.010 mole) of IV in 25 ml. of glacial acetic acid was added dropwise to a stirred solution of 5 ml. of nitric acid (70%; sp. gr. 1.42) in 15 ml. of glacial acetic acid at 23–24°. After 35 minutes, a crystalline precipitate began to form. Stirring was continued for 2 hours. The precipitate was filtered off, washed with glacial acetic acid, and dried by suction. It weighed 0.69 g. (30%) and melted at 175–176°. The filtrate was allowed to stand for 1 hour. No further precipitation occurred. Crystallization of the crude material from ethanol-water gave 0.55 g. (24%) of colorless needles, m.p. 177.5°. Anal. Calc. for  $C_{12}H_{21}NO_3$ : C, 63.4; H, 9.31; N, 6.16; mol. wt., 227. Found: C, 63.5; H, 9.24; N, 6.24; mol. wt., 236.

The same product resulted when IV was treated with an aqueous solution of nitrous or nitric acid, but the yields were much lower.

When a solution of 0.25 g. (0.0011 mole) of  $C_{12}H_{21}NO_3$  in 5 ml. of 95% ethanol was treated with 0.38 g. (0.0055 mole) of hydroxylamine hydrochloride and 0.45 g. (0.0055 mole) of anhydrous sodium acetate a reaction occurred during 36 hours of reflux. Subsequently when water was added 0.03 g. (12%) of original  $C_{12}H_{21}NO_3$  was recovered. Further aqueous dilution precipitated 0.16 g. (64 wt. %) which, crystallized from methanol-water, left 0.10 g. (40 wt. %), m.p. 143–144° with gassing. Anal. Calc. for  $C_8H_{16}NO_2$ : C, 61.1; H, 9.40; N, 8.91; mol. wt., 157. Found: C, 61.5; H, 9.33; N, 8.92; mol. wt., 258.

*2,2,4,4-Tetramethylpentanoic Acid from  $C_{12}H_{21}NO_3$*

(a) *Alkaline Hydrolysis*

When 0.05 g. (0.00022 mole) of  $C_{12}H_{21}NO_3$  was treated with 2 ml. of hot 5% aqueous sodium hydroxide solution the solid slowly dissolved during 20 minutes and ammonia was evolved. The system, cooled and acidified by hydrochloric acid, yielded 0.01 g. (29%), m.p. 40–44°. Crystallization from methanol-water raised this melting point to 44.0–44.5°. A mixture melting point with authentic 2,2,4,4-tetramethylpentanoic acid (20) was not depressed.

(b) *Acid Hydrolysis*

During 12 hours a system comprising 0.56 g. (0.0025 mole) of  $C_{12}H_{21}NO_3$  in 20% hydrochloric acid was boiled under reflux. The resulting yellow oil (0.41 g.) dissolved almost entirely in 5% aqueous sodium hydroxide. The solution, after ether extraction, was acidified to give 0.23 g. (58%) of tetramethylpentanoic acid, m.p. 43.5–44.5°. A mixture melting point was not lowered.

The acidic filtrate, treated with dinitrophenylhydrazine in methanolic hydrochloric acid, yielded a dinitrophenylhydrazone, m.p. 170–172°.

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# NUCLEAR MAGNETIC RESONANCE MEASUREMENTS OF COMPLEXES OF CHLOROFORM WITH AROMATIC MOLECULES AND OLEFINS<sup>1</sup>

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## ABSTRACT

In order to study the effect of association with  $\pi$ -donors, the proton resonance signal of chloroform in the aromatic solvents benzene, toluene, mesitylene, chlorobenzene, *o*-dichlorobenzene, bromobenzene, nitrobenzene and in the olefinic solvents 1-hexene, cyclohexene, and cyclohexadiene was measured as a function of concentration. The observed shifts of the resonance signal are indicative of specific complex formation. In the aromatic solvents benzene, toluene, and mesitylene, complex formation results in an anomalous shift of the chloroform resonance to high field, which can be attributed to a large induced diamagnetism resulting from the circulation of  $\pi$ -electrons in the aromatic ring. An approximate calculation indicates that the chloroform molecule in the complex is oriented with the hydrogen atom near the six-fold axis above the plane of the aromatic ring and the chlorines directed away from the ring. In nitrobenzene this type of association with chloroform gives way to  $n$ -donor association with the oxygen atom of the nitro group. This type of association also occurs to some extent in the halogenated benzenes. A small shift of the chloroform signal to low field is observed with the olefinic solvents, which is attributable to weak  $\pi$ -donor association. Analysis of the freezing-point diagrams of the binary systems with chloroform provide further evidence of complex formation.

Molecular complexes between hydrogen chloride and molecules containing  $\pi$ -orbitals such as olefins, acetylenes, and benzene derivatives have been previously reported (5). The composition of the molecular compounds formed in the solid phase was demonstrated by thermal analysis. To account for the binding forces in these complexes it was postulated that weak hydrogen bonds are formed in which the  $\pi$ -orbitals of the unsaturated hydrocarbons function as donors, in contrast to ordinary hydrogen bonds involving lone pair electron donors ( $n$ -donors). In order to obtain further confirmation of the existence of complexes of this type in solutions of hydrogen chloride in unsaturated hydrocarbons, proton magnetic resonance measurements were undertaken. It was subsequently observed that chloroform behaved similarly to hydrogen chloride both with respect to complex formation with  $\pi$ -donor molecules and with respect to the nature of the chemical shifts derived from proton resonance measurements. Accordingly the greater part of the present work was carried out using chloroform as the acceptor molecule rather than hydrogen chloride. This had the advantage that the measurements could be carried out at room temperature, whereas with hydrogen chloride the measurements must be carried out at low temperatures to avoid excessive pressures.

Nuclear resonance measurements provide a very useful means of studying hydrogen bonding, since it has been demonstrated (1, 11, 12, 4) that the hydrogen involved gives rise to a resonance signal which is shifted to lower field relative to its position in the absence of hydrogen bonding. Thus for example the proton resonance signal of the OH group in ethanol just above its melting point (where almost maximum hydrogen bonding occurs) is shifted to low field by almost five parts per million relative to the signal obtained from a very dilute solution of ethanol in carbon tetrachloride (where complete dissociation is assumed).

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Issued as N.R.C. No. 4223.

<sup>2</sup>N.R.C. Postdoctoral Fellow.



## EXPERIMENTAL

Chloroform was purified by being shaken with water to remove the alcohol added, then dried and fractionally distilled. Mesitylene was distilled, the portion within  $\pm 0.2^\circ$  of the boiling point of  $164.7^\circ\text{C}$ . only being selected. The proton resonance in this purified material was identical with the analytical reagent available commercially. All other chemicals used were standard analytical grade.

The magnetic resonance of the proton was detected on the Varian V-4300 NMR Spectrometer, operating at a constant frequency of 40 Mc./s. Chemical shifts were measured by superimposing an audio-frequency, and using the side bands which develop to determine the shift between two signals in cycles per second (1). A standard external reference capillary of water at room temperature was included in each sample. The sample plus reference capillary were contained in a spinning glass sample tube approximately 6 mm. in inside diameter. Chemical shifts were measured to an accuracy of  $\pm 0.5$  c./s. except at high dilution. The chemical shifts were corrected at each dilution for bulk diamagnetic susceptibility differences, details of which are given in the appendix.

## RESULTS

Preliminary NMR measurements were carried out with solutions of hydrogen chloride in toluene and in mesitylene at low temperatures ( $\sim -50^\circ\text{C}$ .). The proton resonance of hydrogen chloride in these solutions appeared on the *high* field side of the methyl signals of the hydrocarbons, indicating a shift opposite in direction to that anticipated. However, such a result could arise if the hydrogen chloride itself were sufficiently strongly associated. Addition of toluene or mesitylene would then cause dissociation of the hydrogen chloride as well as the formation of complexes with it, the former process however dominating the shift of the proton resonance, which would be to high field. To test this possibility the temperature dependence of the proton resonance in pure liquid hydrogen chloride was measured. This was found to be rather large and hence indicative of moderately strong association. Further confirmation of association was obtained by dilution of the hydrogen chloride with cyclohexane. Again the proton resonance shift of hydrogen chloride was to high field but the shift was only about half as large as in toluene or mesitylene. Hence after allowing for association of hydrochloric acid with itself there remains a net shift to high field of the hydrogen chloride resonance attributable to complex formation with toluene or mesitylene. The origin of this shift, which is opposite in sign to that encountered with ordinary hydrogen bonding, will be discussed below.

In order to eliminate as far as possible the complication of the acceptor molecule (hydrogen chloride) associating with itself, some experiments were carried out using chloroform as the acceptor molecule. Solutions of chloroform in toluene and mesitylene gave rise to a shift of the resonance signal of the chloroform hydrogen to high field with respect to its position in pure chloroform. The shift was not quite as large as the corresponding shift with hydrogen chloride. However the temperature dependence of the pure chloroform signal, and its shift on dilution with cyclohexane, were much smaller indicating less self-association. Accordingly in subsequent measurements, chloroform was used.

The chemical shifts of the chloroform proton (in cycles per second at 40 Mc./s. corrected for bulk magnetic susceptibility) as a function of concentration of chloroform in mesitylene, toluene, benzene, and cyclohexane are plotted in Fig. 1. The chemical shift of the



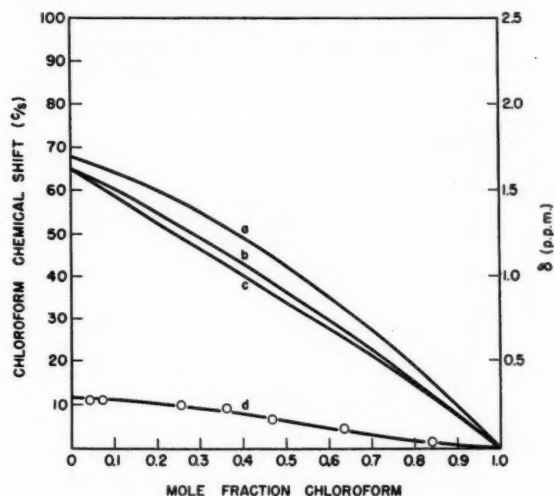


FIG. 1. a. Mesitylene. b. Toluene. c. Benzene. d. Cyclohexane.

proton signal in each solution is shown relative to pure liquid chloroform. In each solution the shift is to higher field with increasing dilution. It is seen that the total shift of the chloroform proton signal in mesitylene, toluene, and benzene is quite large, indicative of complex formation between chloroform and the aromatic hydrocarbons. The corresponding shift in cyclohexane is considerably smaller, the dilution shift amounting to 11 c./s. Since for the present purpose cyclohexane may be regarded as an inert solvent, this shift is a measure of the self-association of pure liquid chloroform, and although it is smaller in magnitude than that of pure liquid hydrogen chloride, it is by no means negligible. Further confirmation of this association was obtained by observing the temperature dependence of the resonance signal in pure chloroform. This was found to shift by 5 c./s. (relative to a cyclopentane external reference) as the temperature was varied from  $-52^{\circ}\text{C.}$  to  $+50^{\circ}\text{C.}$  The possibility of specific interactions in pure chloroform has been previously recognized (6).

Since the dilution shift of the chloroform resonance signal due to self-association will occur in all the solutions studied, this must be corrected for in order to obtain a measure of the shift arising from the interaction of chloroform with the aromatic molecules. The correction was made by subtracting from the chloroform proton shift, measured in benzene, toluene, and mesitylene, at each concentration, the corresponding dilution shift of chloroform in the inert solvent cyclohexane. The corrected shifts are shown plotted against concentration in Fig. 2. The total shifts of the chloroform at infinite dilution in the respective solvents are listed in Table I together with the corresponding corrected shifts. Fig. 3 summarizes the chemical shift data of chloroform (corrected for self-association) in a number of other solvents whose molecules might be expected to exhibit  $\pi$ -donor association with chloroform.

Valuable confirmation of specific molecular association and molecular compound formation can be gained from the freezing-point diagram. Employing procedures previously described (5) freezing point diagrams of the binary systems of chloroform with

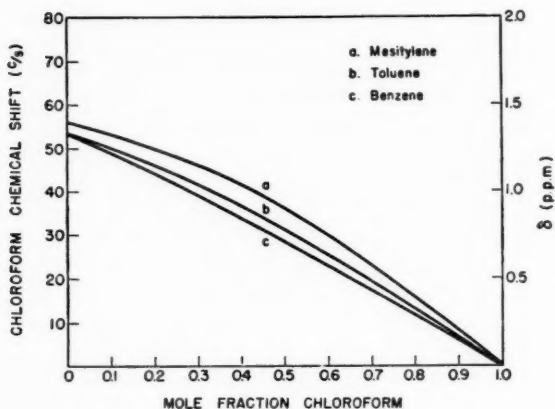


FIG. 2.

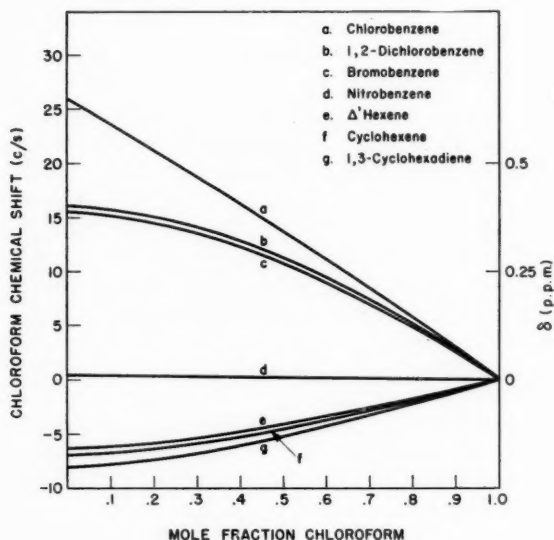


FIG. 3.

each of the aromatic or olefinic solvents were determined. These are shown in Figs. 4, 5, and 6. The melting points of molecular compounds and eutectic temperatures are listed in Table II. Of the three compounds benzene, toluene, and mesitylene, all but benzene show 1 : 1 molecular compounds with chloroform. The high melting point of benzene may obscure a molecular compound in the freezing-point diagram although a molecular compound with benzene is just barely perceptible if the stronger acceptor, hydrogen chloride, is used in place of chloroform (5). None of the other aromatic compounds, chlorobenzene, *o*-dichlorobenzene, bromobenzene, and nitrobenzene, show a molecular compound with chloroform in the freezing-point diagrams. Among the three

TABLE I  
 CHLOROFORM SHIFTS\* AT INFINITE DILUTION

Compounds	Total shift (cycles/second)		Interaction shift† (cycles/second)
	Observed	Corrected‡	
Mesitylene	74.7	68	57
Toluene	72.7	65	54
Benzene	73.7	65	54
Chlorobenzene	42.5	40.5	29.5
<i>o</i> -Dichlorobenzene	20.2	27.3	16.3
Bromobenzene	27.5	26.6	15.6
Nitrobenzene	22.5	11.5	0.5
Cyclohexane	19.0	11.0	0
$\Delta^1$ Hexene	22.5	4.4	-6.6
Cyclohexene	17.2	4.2	-6.8
1,3-Cyclohexadiene	20.5	3.0	-8.0

\*Relative to pure chloroform at 25° C.

†Corrected for differences in diamagnetic susceptibility.

‡Total shift less the shift at infinite dilution in cyclohexane.

TABLE II

	Eutectics		Compounds	
	Composition, mole % chloroform	M.p., °C.	Composition, mole % chloroform	M.p., °C.
Mesitylene	82.5	-73	50	-49
Toluene	22.5	-64.5	50	-106
Benzene	30.0	-115	—	—
Nitrobenzene	73.5	-85	—	—
Bromobenzene	75.5	-80.5	—	—
1,2-Dichlorobenzene	68	-81.5	—	—
Chlorobenzene	77	-74	—	—
Cyclohexene	60	-86	—	—
1,3-Cyclohexadiene	23	-134	—	—
$\Delta^1$ Hexene	31.5	-132.5	—	—
Cyclohexene*	21.5	-134	66.6	-83
	28.0	-124.5	50	-116.5
	81.5	-134.0		

\*Thermal analysis using HCl and cyclohexene.

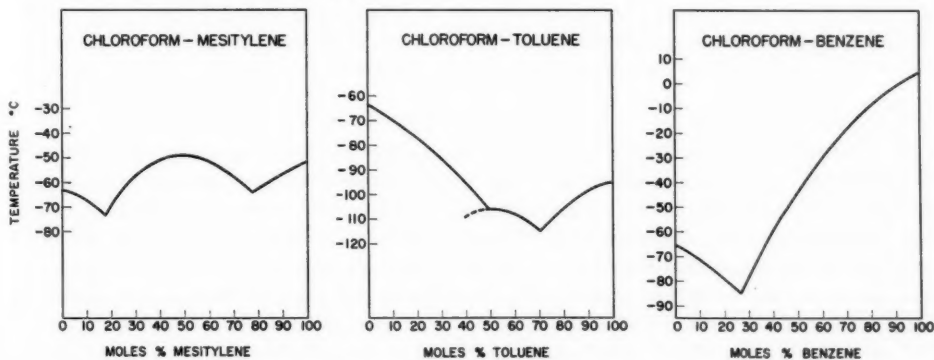


FIG. 4.

olefins 1-hexene, cyclohexene, and cyclohexadiene, only the first gave a molecular compound with chloroform whose composition is 2 : 1 (chloroform to hexene). Absence of a molecular compound in the binary freezing-point diagram does not of course preclude a specific interaction between the components, particularly if such interaction is weak, as it may well be with chloroform. If a stronger acceptor molecule, such as hydrogen chloride, is used in place of chloroform the anticipated molecular compound may appear. This was confirmed in the case of cyclohexene (Fig. 6).

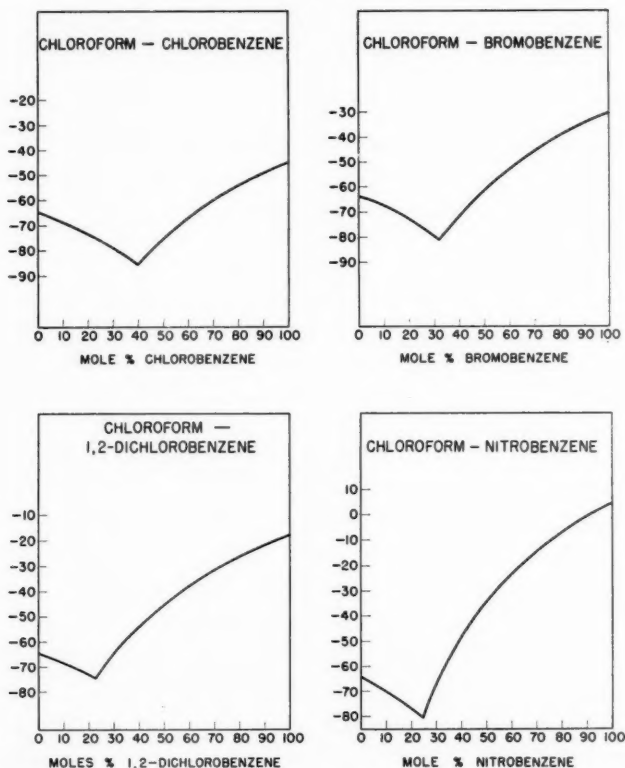


FIG. 5.

## DISCUSSION OF RESULTS

It is evident from Fig. 2 and Table I that even after the "dilution shift" of chloroform is allowed for, there is a large net shift of the NMR signal of the chloroform proton in solution in each of the three solvents benzene, toluene, and mesitylene. This shift, which may be termed the "interaction shift", is to higher magnetic field. This is in sharp contrast to the corresponding shift to low field observed in hydrogen bonding involving lone pair donors, as for example in the alcohols, or in chloroform when the latter is associated with acetone or triethylamine (11). A partial explanation of the different behavior of the chloroform proton resonance in the aromatic solvents may be sought in the magnetic behavior of the aromatic molecules themselves. A molecule such as benzene

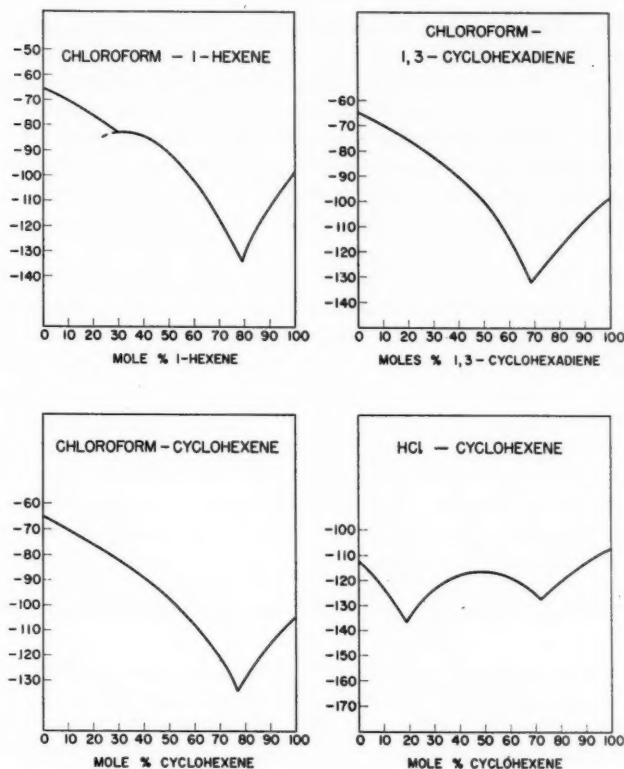


FIG. 6.

has a large diamagnetic anisotropy. Because of its mobile  $\pi$  electrons, in the presence of a magnetic field, a large diamagnetic circulating current is induced in the plane of the aromatic ring (10, 2). The secondary magnetic field due to this "ring" current is such that it reinforces the applied field at a point outside the ring, but in a plane with the ring, and it opposes the applied field at a point above or below the plane of the ring. Accordingly a proton which finds itself in the latter position will have its nuclear magnetic resonance signal displaced to higher field (if the resonance frequency is maintained constant).

It seems very likely therefore that the aromatic "ring" diamagnetism can account for the chloroform proton resonance shift to high field in the aromatic solvents. This implies a specific interaction with the aromatic molecules such that the chloroform hydrogen is preferentially located above or below the plane of the aromatic ring, since if the mutual orientation of the two kinds of molecules were completely random the field enhancement due to the ring current would be considerably smaller. The above preferred orientation is just that to be expected if the chloroform hydrogen interacts with the donor  $\pi$  electrons of the benzene ring. If the chloroform interaction shifts in benzene, toluene, and mesitylene, which amount to an average value of 55 c./s., are interpreted in this manner, this result can then be utilized to obtain a rough measure of

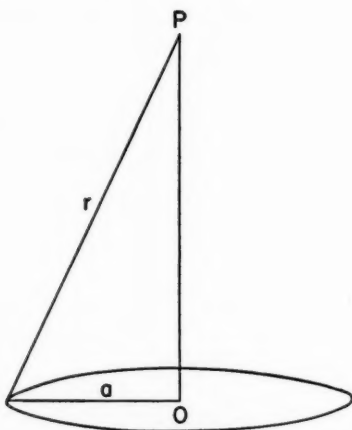
the distance of the chloroform proton from the plane of the aromatic ring in the molecular complex.

In the calculation it is assumed that in the molecular complex the hydrogen atom of the chloroform is above the plane of the aromatic ring in the vicinity of the six-fold symmetry axis. The molecular axis of the chloroform molecule could be parallel with the latter axis, although this is not a necessary assumption. Considering the aromatic ring as a circular loop of radius,  $a$ , equal to  $1.4 \text{ \AA}$ , the current induced by an applied magnetic field,  $H_0$ , is given by (see Ref. 10)

$$[1] \quad i = 3e^2 H_0 / 2\pi m c$$

where  $e$  and  $m$  are the electronic charge and mass,<sup>\*</sup> and  $c$  is the velocity of light. The small field  $H$  on the axis of a circular coil of radius  $a$  at the point  $P$  (as shown in the diagram) is given by

$$[2] \quad \Delta H = 2\pi i a^2 / r^3.$$



Substituting for the ring current,  $i$ , from eq. [1] gives

$$[3] \quad \Delta H / H = 3e^2 a^2 / m c^2 r^3 = \delta,$$

which gives the chemical shift,  $\delta$ , of a proton at  $P$ , expressed in dimensionless units (p.p.m.). Averaging over all orientations of the molecule in the field introduces a factor of  $\cos^2\theta = 1/3$ , so we have finally for the enhanced chemical shift,

$$[4] \quad \delta = e^2 a^2 / m c^2 r^3.$$

Taking the chemical shift due to the ring current as 55 c./s. (see above) or 1.37 p.p.m., the value of  $3.43 \text{ \AA}$  is obtained for  $r$ . The distance  $OP$ , which is the average distance of the chloroform proton from the plane of the ring, is then found to be  $3.1 \text{ \AA}$ . The above calculation is rather approximate, and this figure is perhaps slightly high,<sup>\*</sup> but it supports the general interpretation that the interaction of the aromatic ring is directly

<sup>\*</sup>The assumption that the chloroform proton is on the six-fold axis of the benzene ring may not be justified. Any displacement from this position parallel to the plane of the ring would give a smaller calculated distance.



with the chloroform hydrogen. An alternative mutual orientation of the two molecules where the chloroform molecular axis is also parallel with the six-fold axis of benzene, but with the three chlorine atoms instead of the hydrogen atom situated adjacent to the aromatic ring, appears to be ruled out by the above calculation.

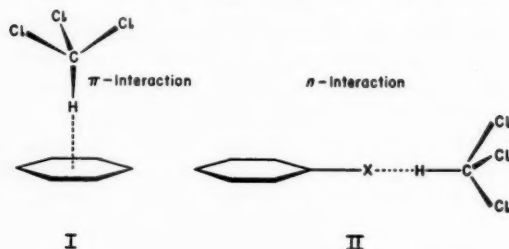
Similar conclusions to the above have also been arrived at independently by Bothner-By and Glick (3), who carried out a detailed study of the effect of volume susceptibility on the proton resonance of certain aliphatic compounds dissolved in aromatic solvents. The latter were found to have an anomalous volume susceptibility due to the induced "ring" diamagnetism, shifting the proton signal on the average by approximately 25 c./s. (no correction was attempted for the "dilution shift" of the aliphatic solute). The shift of the chloroform signal in benzene and toluene was found to be considerably larger than this and was attributed to specific complex formation whereby the chloroform hydrogen is preferentially oriented normal to the plane of the aromatic ring.

Molecular complex formation between chloroform and mesitylene or toluene is confirmed by the freezing-point diagrams (Fig. 4). The nature of the forces involved in the complex is not clear. It has previously been suggested (5) that the complexes formed between  $\pi$ -donor molecules and hydrogen chloride may involve a weak hydrogen bond. Chloroform may be expected to behave similarly with  $\pi$ -donor molecules. Recent infrared measurements by Huggins and Pimentel (8) lend further support to this conclusion. It was found that the intensity of the C—D stretching frequency of chloroform-*d* in various solvents, including benzene and mesitylene, was considerably enhanced, indicating complex formation analogous to hydrogen bonding. Frequency shifts were small or absent.

The above explanation implies that the interaction is primarily electrostatic in nature or arises from strong polarization forces. Charge transfer forces (9) may provide a possible alternative mode of interaction. In this connection the ultraviolet absorption spectra of solutions of chloroform in mesitylene and of hydrogen chloride in mesitylene were measured.\* No absorption resembling a charge transfer spectrum could be found in the near ultraviolet (to 2300 Å), nor was there any noticeable shift of the mesitylene absorption. Consequently the question of whether charge transfer forces are involved or whether the interaction is primarily of electrostatic origin cannot be definitely answered.

The shift of the chloroform hydrogen in solution in the aromatic solvents chlorobenzene, *o*-dichlorobenzene, bromobenzene, and nitrobenzene involves further considerations. It is known that the introduction of electron-withdrawing substituents reduces the  $\pi$ -donor capacity of the aromatic ring. However the induced "ring" diamagnetism should still be operative. From the work of Bothner-By and Glick (3) this should give rise to a maximum shift to high field of about 25 c./s. for the chloroform proton, assuming no specific complex formation. From Table I and Fig. 3 it is seen that only chlorobenzene approaches this expectation; the maximum shifts in *o*-dichlorobenzene and bromobenzene are smaller and in nitrobenzene it is very nearly zero. This can only be accounted for by assuming another type of association with chloroform in which the halogen atoms or the nitro-group of the solvent molecules act as  $n$ -donors for the chloroform hydrogen. The halogen substituents may be expected to be rather weak donors; the oxygen atom of the nitro group should be a much stronger donor. We thus have two possible modes of association, as shown schematically in the following diagram:

\*We are greatly indebted to Dr. Jan Kommandeur for carrying out these measurements.



The NMR measurements are then consistent with the conclusion that in the solvents benzene, toluene, and mesitylene, only complexes of type I ( $\pi$ -donor association) occur. In the solvents chlorobenzene, *o*-dichlorobenzene, bromobenzene, and nitrobenzene complexes of both types I and II may occur although in nitrobenzene type II ( $n$ -donor association) predominates. Possibly because of the high melting point of nitrobenzene, a 1 : 1 molecular compound in the freezing point diagram may be obscured (see Fig. 5).

The interaction shift of chloroform in the olefinic solvents 1-hexene, cyclohexene, and cyclohexadiene is small and to lower field (relative to pure liquid chloroform). Here the anomalous "ring" diamagnetism is absent and hence the observed shift may be regarded as characteristic of chloroform association with an olefinic  $\pi$ -bond. This type of association may be expected to be considerably weaker than, say, the  $n$ -donor association of chloroform in acetone. The chloroform shift (interaction shift) in acetone was observed to be 30.9\* c./s. (11), which is to be compared with an average value of 7 c./s. in the olefinic solvents employed in the present measurements. The freezing-point diagrams (e.g. cyclohexene, Fig. 6) would suggest that with a stronger acceptor molecule such as hydrogen chloride, the NMR shift of the interacting hydrogen may be considerably larger.

#### ACKNOWLEDGMENTS

We wish to acknowledge the assistance of Mr. Yves Lupien in carrying out the freezing point measurements in these systems.

#### APPENDIX

In the present work a small sealed capillary containing water was added to the chloroform solutions being measured. This served as an external reference signal, from which the separation (in cycles per second) of the resonance signal of the chloroform proton was measured. A similar measurement was carried out for pure liquid chloroform, which gave an observed shift of 103 c./s. or 2.58 parts per million relative to the water reference signal which appears at higher field. In order to compare the observed shifts of the chloroform signal in the various solutions measured, a correction for the bulk magnetic susceptibility of the solutions is required. If  $\delta'_{\text{CHCl}_3}$  and  $\delta'_s$  are respectively the observed shift of pure chloroform, and of chloroform in a solution, both measured relative to water (in p.p.m.), the corrected shifts are given by (see Ref. 7)

$$[1] \quad \delta_{\text{CHCl}_3} = \delta'_{\text{CHCl}_3} + \frac{2}{3}\pi(\chi_{\text{CHCl}_3} - \chi_{\text{H}_2\text{O}}),$$

$$[2] \quad \delta_s = \delta'_s + \frac{2}{3}\pi(\chi_s - \chi_{\text{H}_2\text{O}}),$$

\*The infinite dilution shift of 11.5 c./s. in cyclohexane has been added to the value 20.4 c./s., quoted in the paper of Pimentel, Shoolery, and Huggins, to allow for self-association of chloroform itself.

where  $\chi_{\text{H}_2\text{O}}$ ,  $\chi_{\text{CHCl}_3}$ , and  $\chi_s$  are respectively the volume susceptibilities of water, chloroform, and the chloroform solution. The latter was assumed to be additive in the volume fraction of the two components of the binary solution, i.e.,  $\chi_s = v_1\chi_1 + v_2\chi_2$  where  $v_1$  and  $v_2$  are volume fractions.

If the measurements are carried out at a fixed resonance frequency of 40 Mc./s., as in the present work, equations [1] and [2] can be conveniently expressed in terms of frequency units (cycles per second):

$$[1'] \quad \Delta\nu_{\text{CHCl}_3} = \Delta\nu'_{\text{CHCl}_3} + 83.8(\chi_{\text{CHCl}_3} - \chi_{\text{H}_2\text{O}}) \times 10^6,$$

$$[2'] \quad \Delta\nu_s = \Delta\nu'_s + 83.8(\chi_s - \chi_{\text{H}_2\text{O}}) \times 10^6.$$

It was convenient in the present work to refer the chloroform proton signal measured in the various solutions in terms of a net shift relative to the proton signal in pure liquid chloroform. This is obtained simply as the difference of equations [1] and [2] or [1'] and [2'].

Values of the volume susceptibilities were derived largely from the mass susceptibility values given in the International Critical Tables and the Landolt-Bornstein Tables. Since fairly large discrepancies appeared for some compounds, the values used for the present corrections are listed in the following table.

VOLUME SUSCEPTIBILITY DATA

	$\chi \times 10^6$		$\chi \times 10^6$
Water	-0.720	Bromobenzene	-0.722
Chloroform	-0.731	Nitrobenzene	-0.599
Benzene	-0.626	Cyclohexane	-0.631
Toluene	-0.639	Cyclohexene	-0.576
Mesitylene	-0.652*	1,3-Cyclohexadiene	-0.511
Chlorobenzene	-0.708	1-Hexene	-0.525
<i>o</i> -Dichlorobenzene	-0.817*		

\*Estimated using Pascal constants together with the susceptibility values of closely related compounds.

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## THE CONFIGURATION OF GLYCOSIDIC LINKAGES IN OLIGOSACCHARIDES

### III. *O*- $\alpha$ -D-MANNOPYRANOSYL-(1 $\rightarrow$ 2)-*O*- $\alpha$ -D-MANNOPYRANOSYL-(1 $\rightarrow$ 2)-D-MANNOSE<sup>1</sup>

P. A. J. GORIN<sup>2</sup> AND A. S. PERLIN

#### ABSTRACT

A trisaccharide obtained after acetolysis of *Saccharomyces rouxii* mannan is shown to be *O*- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-*O*- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-D-mannose. Methylation and lead tetraacetate oxidation techniques define the positions of the glycosidic linkages. The configurations of the two linkages are determined through use of two novel degradative methods which yield 2-*O*- $\alpha$ -D-mannopyranosyl-D-mannose and 2-*O*- $\alpha$ -D-mannopyranosyl-glycerol, each containing one of the glycosidic linkages of the parent trisaccharide.

An earlier paper (7) described a mannan which was isolated from a fermenting culture of *Saccharomyces rouxii* (15). Two oligosaccharides were obtained after acetolysis of the polysaccharide, one of which was found to be 2-*O*- $\alpha$ -D-mannopyranosyl-D-mannose and the other an amorphous trisaccharide composed of D-mannose units. The latter is now shown to be *O*- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-*O*- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-D-mannose (I).

Methylation of the trisaccharide and hydrolysis of the methylated product yielded two parts of crystalline 3,4,6-tri-*O*-methyl-D-mannose (2), and one part of 2,3,4,6-tetra-*O*-methyl-D-mannose, characterized as the corresponding D-mannonic acid phenylhydrazide (5). The positions of both glycosidic linkages of the trisaccharide are therefore 1,2-.

The compound consumed lead tetraacetate only slowly, and in the potassiumacetate-catalyzed oxidation the trisaccharide and the corresponding triitol each yielded one mole of formaldehyde, in agreement with the formulation of a 1,2-linkage at the reducing end (4). Further, the central D-mannose unit in the triitol consumed 1 mole of lead tetraacetate, as expected for a 1,2- (or 1,4-) linkage, but its rate of oxidation was slow relative to the oxidative attack at the end-units. It has been noted elsewhere (14) that in the glucose and xylose series a *trans*-2,3-diol adjacent to a 1,4-glycosidic linkage is not oxidized by lead tetraacetate. The current results demonstrate a resistance to oxidation also by a *trans*-3,4-diol in a mannose residue adjacent to a 1,2- $\alpha$ -mannosidic linkage.

To determine the configurations of the two glycosidic linkages it was proposed to chemically degrade the trisaccharide and obtain two disaccharides, each containing one of the glycosidic linkages of the parent compound. This approach has been successfully employed, for example, by Wolfrom *et al.* (16) who obtained maltitol and isomaltose by partial hydrolysis of reduced panose, and more recently by Kuhn *et al.* (11), for a trisaccharide from human milk. In the present study, selective degradation of the mannotriose was achieved by the use of novel methods which permitted preferential removal either of the non-reducing end-unit or of the reducing end-unit.

The non-reducing end-unit was removed in the following way. The mannotriose (I) was first reduced with sodium borohydride (17) to an amorphous mannotriitol (II)

<sup>1</sup>Manuscript received November 19, 1956.

Contribution from the National Research Council of Canada, Prairie Regional Laboratory, Saskatoon, Saskatchewan.

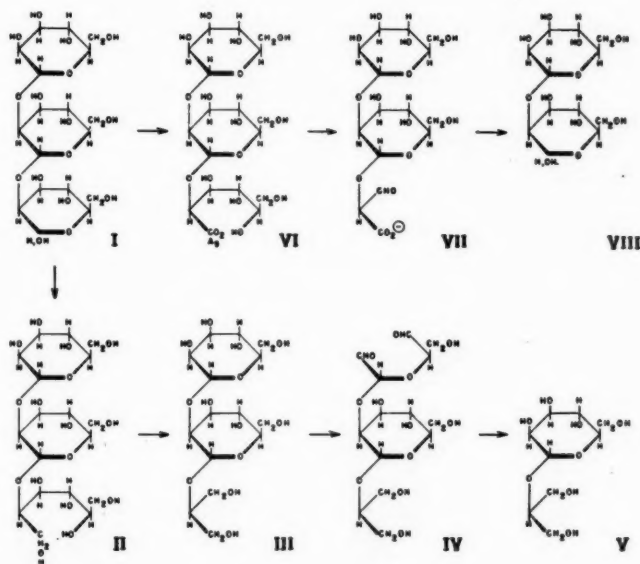
Issued as N.R.C. No. 4219 and as Paper No. 239 on the Uses of Plant Products.

<sup>2</sup>National Research Council of Canada Postdoctorate Fellow, 1955-57.

characterized as its duodecabenzoate. This was then treated with 3 moles of lead tetraacetate, and the oxidation product reduced with sodium borohydride to give an amorphous mannosyl-glycerol (III), which yielded a solid nona-*p*-nitrobenzoate. These steps are analogous to the stepwise degradation of 2-*O*- $\alpha$ -D-mannopyranosyl-D-mannose (3). The mannosyl-glycerol (III) was then oxidized with two moles of lead tetraacetate which, in agreement with the results noted above, preferentially attacked the terminal D-mannose unit and produced the dialdehyde (IV). Treatment of this product with phenylhydrazine acetate according to the method of Barry (1) afforded 2-*O*- $\alpha$ -D-mannopyranosyl-glycerol (V) (3) characterized as its hexa-*p*-nitrobenzoate derivative. The 1,2-glycosidic linkage between the central residue and the reducing end-unit was thus found to possess the  $\alpha$ -configuration.

Partial hydrolysis of oligosaccharide osazones has been suggested as a possible means for preferential removal of reducing end-units (6). However, this method was not applicable to the mannotriose, which cannot form an osazone. An alternative method for the reducing end-unit was therefore developed. The trisaccharide was oxidized with bromine water in the presence of calcium benzoate (10) to the mannosyl-mannonic acid isolated as the silver salt (VI), which in turn was oxidized with 3 moles of lead tetraacetate to give presumably a salt of *O*- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-*O*- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-L-glycerotriuronic acid (VII). Treatment of the latter with hot dilute acetic acid readily hydrolyzed off the tartronic semialdehyde residue, affording 2-*O*- $\alpha$ -D-mannopyranosyl-D-mannose (VIII), characterized by reduction with sodium borohydride to crystalline 2-*O*- $\alpha$ -D-mannopyranosyl-D-mannitol (7). It was evident, therefore, that the glycosidic linkage between the non-reducing end-unit and the central residue of the trisaccharide also possesses the  $\alpha$ -configuration.

As previously noted (7), the disaccharide, 2-*O*- $\alpha$ -D-mannopyranosyl-D-mannose, represents 10% of the polysaccharide, and the present trisaccharide, 25%. The high





total yield obtained of these two compounds shows that the 1,2-glycosidic linkages in the polymer have predominantly, if not entirely, the  $\alpha$ -configuration. The configuration of the 1,6-linkage, the other major type present, is yet to be determined.

#### EXPERIMENTAL

Evaporations were carried out under reduced pressure at 40° C. Optical rotations were measured at 27° C. All melting points are uncorrected. Paper chromatograms were developed using Whatman No. 1 filter paper, *n*-butanol-ethanol-water (40:11:19 v/v) as solvent, and *p*-anisidine hydrochloride (9) and ammoniacal silver nitrate (12) as spray reagents.

##### *Positions of Linkage in the Trisaccharide*

The mannotriose (298 mg.) ( $[\alpha]_D +55^\circ$ , *c*, 1.5, water) was methylated six times with aqueous sodium hydroxide - methyl sulphate. After destruction of excess methyl sulphate the aqueous solution was neutralized using acetic acid and then extracted continuously with chloroform. The extract was dried over magnesium sulphate, filtered, and evaporated to a sirup (301 mg.) which was distilled rapidly at 1 mm. pressure. The product (181 mg.) was heated at 100° C. for 18 hours in 90% formic acid (5 ml.). The hydrolyzate was then concentrated to a sirup which was dissolved in water and heated at 100° C. for 30 minutes, the procedure being repeated three times.

The mixture of *O*-methyl sugars, which on paper chromatographic examination was shown to contain no di-*O*-methyl mannose, was fractionated on a cellulose column (8). Benzene-ethanol-water (10:1:trace, v/v) eluted the tetra-*O*-methyl component (53 mg.),  $[\alpha]_D +25^\circ$  (*c*, 1.7, methanol). Oxidation of this sugar by bromine water, followed by lactonization and treatment of the lactone with an equivalent of phenylhydrazine in refluxing ethanol, yielded, after three recrystallizations from benzene, 2,3,4,6-tetra-*O*-methyl-D-mannonic acid phenylhydrazide. The substance had m.p. and mixed m.p. 180°-181° C. and gave an X-ray diffraction pattern identical with that of an authentic specimen. Calculated for  $C_{16}H_{26}O_6N_2$ :  $-OCH_3$ , 36.2%. Found:  $-OCH_3$ , 35.8%.

The tri-*O*-methyl fraction was eluted by benzene-ethanol-water (7:1:trace, v/v) and crystallized on evaporation of the solvent; yield, 97 mg. After recrystallization twice from ether the product (51 mg.) had m.p. 95°-99° C. undepressed on admixture with authentic 3,4,6-tri-*O*-methyl-D-mannose and  $[\alpha]_D +20^\circ \rightarrow +7^\circ$  (constant value; *c*, 1.15, water). The infrared spectrum of the product was identical with that of the known material. Calculated for  $C_9H_{18}O_6$ : C, 48.64%; H, 8.16%. Found: C, 48.92%; H, 8.11%. Only 18 mg. of the product could not be induced to crystallize.

A sample of the trisaccharide was treated with excess lead tetraacetate in acetic acid. The consumption of reagent, moles per mole, after 5, 31, and 55 minutes was 0.03, 0.27, and 0.42, respectively. In 90% acetic acid and in the presence of potassium acetate, lead tetraacetate oxidation (13) liberated 1.0 mole of formaldehyde per mole in 1 hour's reaction time.

##### *O*- $\alpha$ -D-Mannopyranosyl-(1 $\rightarrow$ 2)-*O*- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-D-mannitol

The mannotriose (683 mg.) was treated with sodium borohydride (200 mg.) in water (20 ml.) for 18 hours. The solution was acidified with acetic acid, treated with Amberlite IR-120, and then concentrated to a solid. The latter was dissolved in methanol, which was evaporated off. This process was repeated three times to give the amorphous mannotriitol (674 mg.) which had  $[\alpha]_D +49^\circ$  (*c*, 0.8, water). On oxidation of the mannotriitol with



lead tetraacetate in 90% acetic acid containing potassium acetate the production of formic acid was constant in 40 minutes' reaction time at 2.3 moles per mole; the consumption of lead tetraacetate was 5.0 moles per mole. These values corresponded to oxidation of the two end-units, which would require 2.6 moles of formic acid (13) and 5.0 moles of lead tetraacetate per mole. During the next 1.5 hours the consumption of oxidant increased to 5.7 moles per mole, and a further 1 hour's reaction time raised the value to 5.8 moles per mole. This slow oxidation without further production of formic acid was interpreted as involving the central D-mannose unit. The yield of formaldehyde was 0.9 moles per mole (requires 1.0 mole per mole).

The manntriitol (30 mg.) was benzoylated in a mixture of pyridine (0.20 ml.), benzoyl chloride (0.13 ml.), and chloroform (0.30 ml.). After 3 hours at room temperature the sugar had dissolved and the reaction mixture was added to chloroform, which was washed with 0.1 N sulphuric acid, aqueous sodium bicarbonate, and water successively, dried over magnesium sulphate, filtered, and evaporated to a white solid. The duodecabenzoate was purified by two precipitations from methanol. Yield 53 mg., m.p. 96°–98° C., and  $[\alpha]_D -4^\circ$  (c, 0.8, chloroform). Calculated for  $C_{102}H_{81}O_{28}$ : C, 69.36%; H, 4.65%. Found: C, 69.81%; H, 4.65%.

*O- $\alpha$ -D-Mannopyranosyl-(1 $\rightarrow$ 2)-O- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-glycerol*

The manntriitol (516 mg.) was dissolved in water (2 ml.), acetic acid (200 ml.) added, and the mixture treated with lead tetraacetate (1.35 g., 3.0 molar equivalents). After 18 hours lead was precipitated as lead oxalate by the addition of oxalic acid and the solution was filtered. The filtrate was evaporated to dryness and the residue was dissolved in water (50 ml.) containing sodium borohydride (500 mg.). After 1 hour the reaction mixture was worked up as described above. The amorphous mannobiosylglycerol thus formed (294 mg.) had  $[\alpha]_D +49^\circ$  (c, 1.4, water) and acid hydrolysis of the material gave mannose and glycerol which were detected on a paper chromatogram.

The glycerol derivative (45 mg.) was heated at 80° C. for 30 minutes in pyridine (1.7 ml.) containing *p*-nitrobenzoyl chloride (280 mg.). The precipitate which formed on addition of the reaction mixture to aqueous sodium bicarbonate was filtered off after 30 minutes and reprecipitated from acetone-ethanol. The amorphous white nona-*p*-nitrobenzoate (60 mg.) had m.p. 128°–131° C. and  $[\alpha]_D -3^\circ$  (c, 0.8, chloroform). Calculated for  $C_{78}H_{66}O_{40}N_9$ : C, 53.29%; H, 3.15%. Found: C, 53.03%; H, 3.20%.

The mannobiosylglycerol was oxidized with lead tetraacetate in acetic acid containing a trace of water. The reaction was very slow, only 0.16 and 0.90 mole per mole being consumed after 2 and 20 hours respectively.

*2-O- $\alpha$ -D-Mannopyranosyl-glycerol*

Mannobiosylglycerol was oxidized with lead tetraacetate under the conditions mentioned immediately above except that the proportion of water in the reaction mixture was increased.

The sugar (248 mg.) was dissolved in water (1 ml.) and made up to 50 ml. with acetic acid to which lead tetraacetate (560 mg.; 2.1 molar equivalents) was added. After 18 hours all of the reagent had been consumed and 10% oxalic acid in acetic acid (1.3 ml.) was added. The precipitate which formed was filtered off and the filtrate evaporated to dryness. The residue was dissolved in water (25 ml.) containing phenylhydrazine (1 ml.) and acetic acid (1 ml.) and the solution heated at 100° C. for 30 minutes. The mixture was evaporated to a sirup, which was dissolved in aqueous ammonia. The solution was

extracted twice with chloroform, treated with Amberlites IR-120 and IR-4B, and evaporated to a sirup (122 mg.). The material was fractionated on a cellulose column using *n*-butanol saturated with water as the mobile phase. 2-*O*- $\alpha$ -D-Mannopyranosyl-glycerol (42 mg.) was isolated as a sirup and identified by its infrared absorption spectrum and its  $[\alpha]_D$ , which was  $+59^\circ$  (*c*, 1.4, water) (3).

The mannosyl-glycerol (28 mg.) was converted to its hexa-*p*-nitrobenzoate derivative by the method described above. The product (60 mg.), which was precipitated twice from ethanol-acetone, had m.p.  $108^\circ$ – $110^\circ$  C.,  $[\alpha]_D -71^\circ$  (*c*, 0.7, chloroform) and an infrared absorption spectrum identical with that of the  $\alpha$ - but not the  $\beta$ -anomer. Calculated for  $C_{61}H_{36}O_{26}N_6$ : C, 53.31%; H, 3.15%. Found: C, 53.17%; H, 3.12%.

#### 2-*O*- $\alpha$ -D-Mannopyranosyl-D-mannose

The mannatriose (373 mg.) was oxidized with bromine (0.04 ml.) in water (25 ml.) containing calcium benzoate (300 mg.). After 3 days the solution did not reduce Fehling's solution and bromine was aerated off. The solution was treated with Amberlite IR-120, extracted three times with chloroform, and then neutralized with silver carbonate. The insoluble material was filtered off and the filtrate evaporated to a small volume. Addition of an excess of ethanol precipitated a white powder, presumably the silver salt of the trisaccharide aldonic acid, which was isolated. Yield 251 mg.

A sample of the product was oxidized with lead tetraacetate in 99% acetic acid. The observed rate of oxidation was as follows:

Time, min.	0	4	13	30	55	125	185
Reagent uptake, moles per mole	0	1.7	2.6	3.2	3.5	4.0	4.2

This relatively rapid uptake of slightly over 3 moles per mole of reagent, which was followed by a slower oxidation, corresponded to the formation of a good proportion of the expected *O*- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-*O*- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-L-glycero-triuronic acid.

Therefore the silver salt (230 mg.) was dissolved in water (2 ml.) to which acetic acid (200 ml.) was added, and the mixture treated with lead tetraacetate (500 mg.; 3 molar equivalents). After 18 hours the solution was evaporated to a solid mass, which was dissolved in water, and 10% oxalic acid in acetic acid (1.1 ml.) added. The solution was filtered and water was added until the volume was 40 ml. Acetic acid (4 ml.) was added and the solution was heated at  $100^\circ$  C. for 1 hour. It was then shown to contain a material which gave a spot on a paper chromatogram corresponding to 2-*O*- $\alpha$ -D-mannopyranosyl-D-mannose.

The solution was evaporated to dryness and the residue was reduced with sodium borohydride (200 mg.) in water (20 ml.). After 18 hours the reaction mixture was worked up as described above and the product was purified by chromatography on a cellulose column using ethyl acetate-acetic acid-water (9:2:2, v/v). Yield 107 mg. Four recrystallizations from ethanol-methanol gave a product with  $[\alpha]_D +36^\circ$  (*c*, 1.0, water) and m.p.  $136^\circ$ – $137^\circ$  C., undepressed on admixture with 2-*O*- $\alpha$ -D-mannopyranosyl-D-mannitol. The crystals gave an infrared absorption spectrum and an X-ray diffraction pattern identical with those of the known compound. Calculated for  $C_{12}H_{24}O_{11}$ : C, 42.10%; H, 6.48%. Found: C, 41.94%; H, 6.52%.

An attempt to degrade the hydroxy-malondialdehyde derivative, prepared by careful lead tetraacetate oxidation of the reducing end-unit of the trisaccharide, using the conditions as for the corresponding *glycerotriuronic acid* derivative (VII), was unsuccessful.

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# THE SECOND VIRIAL COEFFICIENT OF CARBON DIOXIDE AT LOW TEMPERATURES<sup>1</sup>

D. COOK<sup>2</sup>

## ABSTRACT

The fixed volume expansion method for gas compressibility measurements previously employed under conditions of high temperature and high pressure has now been developed for low temperature and low pressure measurements. A sensitive diaphragm null-pressure detector, operating as a capacitor, has been incorporated into the gas pipettes, and eliminates troublesome dead space corrections. The advantages and limitations of the method are discussed. Measurements of the second virial coefficient of carbon dioxide in the temperature range  $-60^{\circ}\text{C.}$  to  $+30^{\circ}\text{C.}$ , and in the pressure range 0.5 to 2.5 atmospheres, are reported.

## INTRODUCTION

Previous measurements in these laboratories of the compressibilities of gases by the expansion method have been made in the pressure region of 60 to 70 atm. and from  $0^{\circ}$  to  $700^{\circ}\text{C.}$ , using an expansion technique. From these measurements the second, third, and in some cases the fourth virial coefficients, as well as the intermolecular force parameters, have been evaluated for a number of gases. One disadvantage of the above method is the elaborate computational procedure required for deriving the virial coefficients from the primary measurements when higher coefficients are involved. The method, as previously employed, is also not very suitable for low temperature measurements. For these reasons an attempt was made to develop an expansion method which could be used at low temperatures and low pressures by means of which the second virial coefficient could be easily derived. By working at low pressures the higher virial coefficients can usually be neglected and this greatly simplifies the analysis of the data. The present paper describes an apparatus designed for compressibility measurements of gases from  $+200^{\circ}\text{C.}$  to  $-180^{\circ}\text{C.}$  in the pressure range 0.5 to 2.5 atmospheres. Measurements of the second virial coefficient of carbon dioxide from  $+30^{\circ}\text{C.}$  to  $-60^{\circ}\text{C.}$  are reported.

## APPARATUS

One of the disadvantages of the high pressure apparatus used hitherto has been the necessity of making dead space corrections for that part of the gas sample in the lines leading to the mercury U tube which must be outside the thermostat. This U tube is the means of balancing the pressure in the gas sample with the externally applied pressure. With this arrangement, too, there is always the risk that mercury may be forced over into the high pressure cell. To avoid these difficulties a sensitive diaphragm was used as the pressure sensitive device and null detector. This has the advantage that it can be incorporated into the equilibrium cell, thus eliminating dead space corrections.

Fig. 1 shows a diagram of the equilibrium cell. It was made of K Monel, and consists of a large pipette *A*, of about 1000 cm.<sup>3</sup> capacity connected to a smaller pipette of about 63 cm.<sup>3</sup> capacity. Valves  $V_1$  and  $V_2$  control the filling of the cell and evacuation of the small pipette after expansion.

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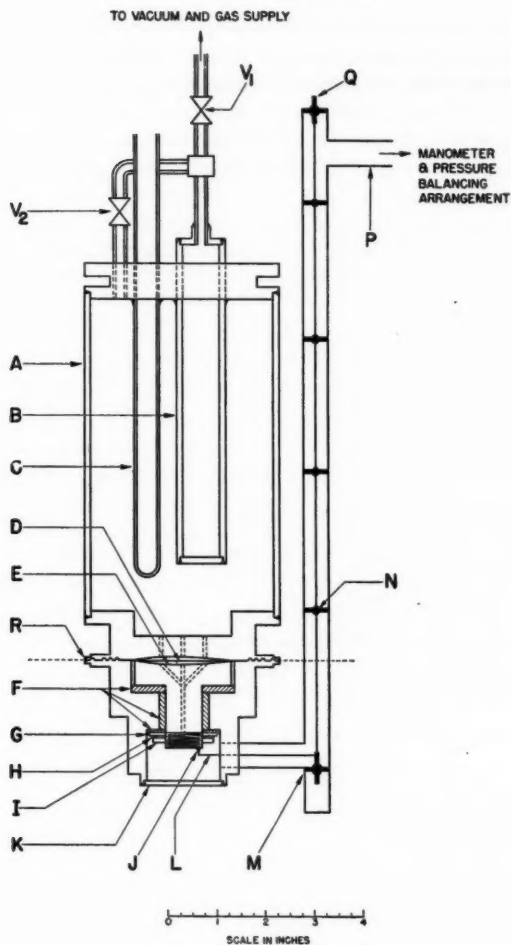


FIG. 1. The diaphragm cell.

The lower half of the cell (below the diaphragm *D*) contains the capacitance probe *E*, insulated from the outside of the cell by quartz insulators *F*. A metal nut *I*, tightening on a crimped spring washer *H*, backed by a flat metal washer *G*, held the probe assembly together. Holes drilled through parallel to the axis permitted the flow of gas. A pin *J* supported a wire *L*, which was mounted coaxially with the tube *M* being supported with glass disks *N* as insulators. The tube *M* serves as the lead to the manometer and pressure balancing device and also provides a shielded lead for the wire *L*, the other end *Q* connecting to the capacitance bridge. The lid *K* was soft-soldered in position after assembly of the probe unit.

#### *The Diaphragm*

Construction of the diaphragm involves a compromise between two opposing factors. For maximum sensitivity the thinner the diaphragm the better. For minimum hysteresis (maximum zero stability) a thicker diaphragm is preferable. Accordingly a 4 in. diameter

K Monel diaphragm, thickness 0.006 in., was made embodying the following features. Three 0.010 in. corrugations were pressed in the diaphragm at radii  $1\frac{3}{8}$  in.,  $1\frac{1}{2}$  in., and  $1\frac{5}{8}$  in. to give added strength, while at a radius of  $1\frac{7}{8}$  in. a 0.015 in. groove was pressed to serve as a locating groove. Corresponding locating grooves were machined on each half of the diaphragm holder. The peaks of the latter grooves were displaced 0.010 in. towards the periphery to stretch the diaphragm slightly. This procedure and the corrugations served to ensure that no "oil can" effects developed in the diaphragm. The forming of the diaphragm was accomplished using a masonite die, on which the corrugation profile was accurately machined, in conjunction with a hard rubber (100 durometer hardness) disk in a steel cup. A hydraulic press requiring about 20 tons pressure was needed to form the corrugations.

Mounting the diaphragm in the cell presented some difficulty. It was hoped that it would be possible to weld the diaphragm into the cell by making the flanges at  $R$  very thin so that the minimum of heat need be applied. However, several test strips proved that the amount of heat required to weld the diaphragm satisfactorily was enough to alter its elastic properties. Even with silver brazing the diaphragm became quite brittle and cracked in several places, as did the quartz insulators. Ultimately soft-soldering provided a satisfactory method, but naturally limited the temperature range over which the cell could be used. After the diaphragm was soldered it was considered advisable to leave four small clamps in place for added support.

The ends of the two halves of the cell next to the diaphragm were made with a curved surface (exaggerated in Fig. 1). This amounted to 0.003 in. at the center, or a radius of 45 ft. This had the effect of making a small pressure change (diaphragm displacement) show as large a capacitance change as possible. To achieve this curvature a series of steps about 0.0003 in. in height were cut on the face and the ridges polished off with a fine paper. The surface was gauged afterwards and found to be very close to the required curvature.

In practice it was necessary to calibrate the diaphragm null point,  $C_0$ , in terms of zero deflection capacitance at zero pressure difference (both sides of the diaphragm connected together) as  $C_0$  is a function of both temperature and pressure. At lower temperatures  $C_0$  increases as the cell contracts. At higher pressures it decreases. Calibration was effected by allowing gas to flow into both halves of the equilibrium cell and the manometer, and taking measurements of total pressure and  $C_0$  at intervals of about 30 cm. Hg. The isotherms of  $C_0$  against pressure so obtained were linear, but the slope varied slightly with temperature. It was usual to check  $C_0$  two or three times in the course of one series of expansions. After several deflections of the diaphragm the zero stability appeared to be of the order of 0.1  $\mu\mu\text{f.}$  (the total zero deflection capacitance of the diaphragm was about 400  $\mu\mu\text{f.}$ ). The sensitivity was of the order of 0.1 cm. Hg per  $\mu\mu\text{f.}$

Capacitances were measured on a General Radio Type 716-C capacitance bridge together with a Type 1231-B amplifier and null detector. The bridge was graduated in units of 0.2  $\mu\mu\text{f.}$  but could be interpolated to 0.02  $\mu\mu\text{f.}$  A standard frequency of 1 kc. was used throughout the measurements after passing through a General Radio Type 1231-P6 filter. Connections from the bridge to the probe in the cell were made using low capacitance shielded cable. All terminals were properly shielded.

#### *Cell Thermostat and Temperature Measurement*

At temperatures below room temperature a double Dewar arrangement proved satisfactory. The inner Dewar contained methanol and was adequately stirred. The



outer Dewar contained solid  $\text{CO}_2$  and methanol for operating temperatures down to about  $-40^\circ\text{C}$ .; below this, liquid nitrogen was used. The temperature sensitive element for temperature control was a metal sheathed platinum resistance thermometer. The bridge and photocell circuit has been described previously (6). It is estimated that this arrangement gives control to  $\pm 0.005^\circ\text{C}$ . but on account of the large thermal capacity of the cell its temperature variation is probably about  $\pm 0.002^\circ\text{C}$ .

#### *The Manometer*

Standard wall Pyrex glass tubing of 1 in. internal diameter was used to construct a manometer 2 meters long. It was designed so that the two mercury menisci were vertically above one another by means of a crossover. It was filled with clean twice-distilled mercury. The upper limb was kept permanently evacuated. The manometer was housed in a thermostat containing well-circulated oil whose temperature was controlled with a sensitive mercury thermoregulator. The temperature variation of the oil was  $\pm 0.005^\circ\text{C}$ .; however the large thermal capacity of the mercury (about 400 cm.<sup>3</sup>) may make the variation somewhat less than this figure. Connections to the manometer made it possible to raise or lower the balancing pressure quickly. A fine adjustment permitted pressure changes of the order of 0.001 cm. Hg to be made.

A 2 meter stainless steel bar, made and calibrated by the Gaertner Scientific Corporation, was used for measuring the height of the mercury column. The graduations were in centimeters and millimeters. It was freely suspended inside the manometer thermostat and used as a guide to line up the manometer into a vertical position. A  $2\frac{1}{2}$  meter cathetometer with vernier attachment was used to interpolate between the millimeter divisions of the 2 meter bar. It was adjusted to the vertical by means of a plumb line. To eliminate vibration both manometer and cathetometer were bracketed to a 2 ft. thick main wall with large iron plates.

#### OPERATION OF THE APPARATUS

The expansion method and technique has been described elsewhere (5), so only brief details will be given here. The method of using the diaphragm is new and a description of the technique of handling it follows:

Because of the variation of the diaphragm "zero" (the value of the capacitance with the pressure equalized on both sides of the diaphragm) with temperature and pressure, it was necessary to calibrate this before each run. To determine this calibration curve, the cell including all the leads, and the manometer, were thoroughly evacuated using a mercury diffusion pump. The gas under investigation was then allowed to flow into the cell, lines, and manometer. At intervals of about 30 cm. Hg the gas flow was stopped and the pressure and capacitance measured after equilibrium was reached. A calibration curve could then be drawn up, which always proved to be linear.

The apparatus was then ready for a series of expansions to be carried out. After each expansion into the small pipette the pressure was adjusted to rough balance as quickly as possible, the new pressure then giving a new capacitance. Adjusting the bridge to this new value enabled the fine pressure adjustment to be carried out. After the final expansion on any particular isotherm, the pressure was equalized on both sides of the diaphragm (by means of an interconnecting valve, not shown on Fig. 1) and readings of pressure and capacitance taken. The point so obtained nearly always lay on, or very near, the original calibration curve.

The time taken to reach equilibrium varied, depending on the temperature. At the

higher temperatures about 15 to 20 minutes was generally sufficient. At lower temperatures this had to be extended to about 30 to 40 minutes.

#### MATERIALS USED

Carbon dioxide as supplied by the Mathieson Company was transferred to an all-metal storage bomb fitted with a high pressure valve. During this process it was sublimed twice between two glass traps with continuous pumping. Its estimated purity was greater than 99.9% CO<sub>2</sub>.

#### RESULTS

The equation of state of a gas may be written

$$[1] \quad pV/RT = 1 + B_T^*/V + C_T^*/V^2 + \dots$$

where  $B_T^*$  and  $C_T^*$  are the virial coefficients. However it is equally permissible over a limited pressure range to use the equation

$$[2] \quad pV = A_T + B_T p + C_T p^2 + \dots$$

The two sets of virial coefficients are related as follows:

$$[3] \quad B_T^* = B_T, \quad C_T^* = RTC_T + B_T^2.$$

For interpreting data derived from the expansion method, equation [2] is best used in the form

$$[4] \quad p_1/p_2 = N + p_1(N-1)B_T/A_T + p_1^2(N-p_2/p_1)C_T/A_T + \dots$$

where  $p_1$  and  $p_2$  are the pressures before and after expansion respectively, and  $N$  is a ratio of the volumes of the two pipettes.

Equation [4] shows that if  $C_T$  is negligible a plot of the pressure ratio against the pressure should give a straight line whose intercept is  $N$  and whose slope is related to the second virial coefficient. Any contribution from the third virial coefficient would be largest at low temperatures and where the pressure approached the condensation pressure. Although there was a very slight indication of some curvature on the  $-60^\circ\text{C}$ . isotherm, no other isotherm showed this. Hence it must be concluded that because of the small size of the deviation from linearity and the nature of the scatter of the points there would be no justification for evaluating a third virial coefficient from these measurements. Accordingly, the method adopted for evaluation of the second virial coefficients was the simple linear least squares method.

Fig. 2 shows the isotherms of  $p_1/p_2$  against pressure. The value of  $N$  was not predetermined but Fig. 2 and Table I show the intercepts to be confined to a small range. Table I

TABLE I

$T$ ( $^\circ\text{C}$ .)	$-10^3 B_T$ (Amagat)	$-B$ (cm. <sup>3</sup> mole <sup>-1</sup> )	$N$
+30	$5.7_0 \pm 0.5_3$	$127 \pm 13$	$1.06317 \pm 0.00004$
0	$7.5_3 \pm 0.3_4$	$168 \pm 8$	$1.06315 \pm 0.00003$
-25	$9.1_6 \pm 0.5_4$	$204 \pm 12$	$1.06310 \pm 0.00004$
-40	$11.9_3 \pm 0.5_0$	$266 \pm 11$	$1.06328 \pm 0.00005$
-50	$13.5_6 \pm 0.6_7$	$302 \pm 15$	$1.06330 \pm 0.00007$
-60	$13.9_2 \pm 0.3_1$	$310 \pm 7$	$1.06320 \pm 0.00003$

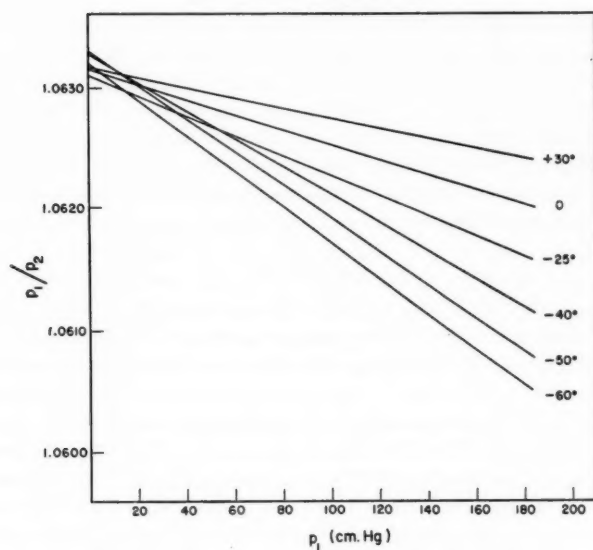
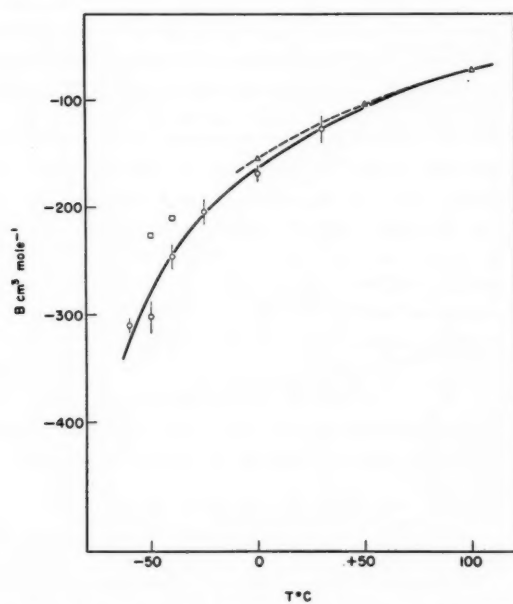


FIG. 2. Isotherms of pressure ratio against pressure.

FIG. 3. Second virial coefficient of CO<sub>2</sub>. ○ Present measurements; △ Reference (2); □ Reference (4).

shows the values of  $N$  and  $B_T$ , the latter being given in Amagat units and also in  $\text{cm}^3 \text{ mole}^{-1}$ . Amagat units can simply be changed to  $\text{cm}^3 \text{ mole}^{-1}$  by multiplying by the normal volume of  $\text{CO}_2$  (viz., the volume of 1 mole of gas at 1 atm. and  $0^\circ \text{C.} = 22265 \text{ cm}^3 \text{ mole}^{-1}$ ). Standard errors in  $N$  and  $B_T$  were derived by the method described by Margenau and Murphy (3).

The virial coefficients thus obtained are shown graphically in Fig. 3 plotted against temperature. Also plotted are the high temperature points previously obtained, and some low temperature points of Schäfer (4).

#### DISCUSSION

In the region where the previous data on  $\text{CO}_2$  and the present measurements overlap, the agreement is almost within the experimental error. Although no standard errors were available for the high temperature work this was thought to be accurate to about 0.5 to 1% or about 1 to 2  $\text{cm}^3 \text{ mole}^{-1}$ . The present method is not as accurate as this, but it should be pointed out that the results having the least confidence in the high pressure method are those in the region of the critical temperature, i.e., around  $30^\circ \text{C.}$  However, a recent investigation of the compressibility of  $\text{CO}_2$  at  $0^\circ \text{C.}$  gives a value of  $B$  of  $-152 \text{ cm}^3 \text{ mole}^{-1}$ . This is the best value from a series of measurements (1). The normal volume derived from the latter work is  $22262.6 \text{ cm}^3 \text{ mole}^{-1}$ , in good agreement with that used by MacCormack and Schneider (2). The only other low temperature values are those of Schäfer (4), also indicated in Fig. 2. Schäfer's results and the present data also agree within the experimental error at  $0^\circ \text{C.}$ , but at lower temperatures our data seem to be significantly lower.

A critical survey of the accuracy of the method is difficult. To give some idea of the scatter in the experimental points these are plotted for a typical isotherm in Fig. 4. Naturally the scatter gets worse at low pressures. For this reason the expansions down any particular isotherm were stopped at about 50 cm. Hg. It is felt that temperature

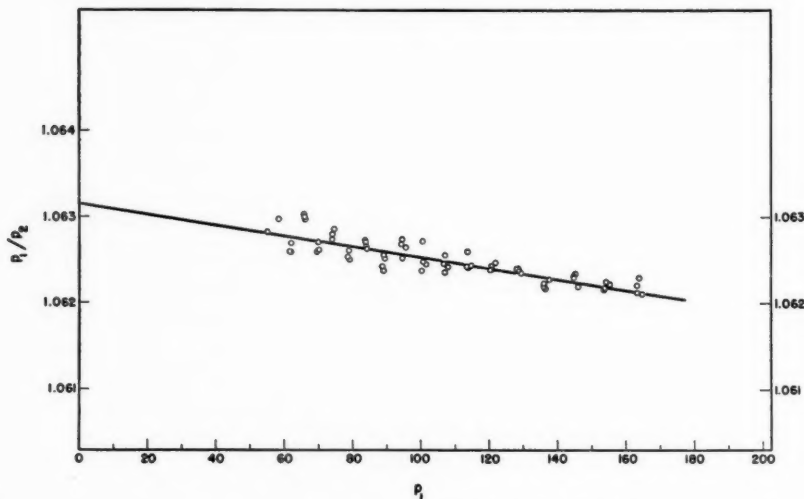


FIG. 4. Experimental points for a typical isotherm.

fluctuations in either the cell thermostat or the manometer thermostat would be too small to have any significant effect on the measured pressure. A simple calculation shows that a variation in the cell thermostat of  $0.002^{\circ}\text{C}$ . would produce a pressure change of the order of 1 in  $10^5$ . The pressure change due to a manometer thermostat temperature change of  $0.005^{\circ}\text{C}$ . would be of the same order. Since no volume measurements are made using the expansion technique, the remaining variable is the pressure. It is probably in the measurement of this variable that the greatest error lies.

Whereas with a piston gauge, as used in the high pressure method, a precision of about 1 in  $2 \times 10^5$  can be obtained at 40 atm., the present low pressure method has a precision of about 1 in  $2 \times 10^4$  at 100 cm. Hg (40 atm. and 100 cm. Hg are approximately half way down the  $p_1/p_2$  against  $p_1$  isotherm for the high pressure and low pressure method respectively). This order of precision in the pressure measurements is able to account very closely for the standard deviation of the value of  $p_1/p_2$  at any given  $p_1$ , which is of the order of 0.00012.

The method offers good possibilities of measuring second virial coefficients to the order of accuracy of about  $\pm 10$  to  $15\text{ cm}^3\text{ mole}^{-1}$ . The operation of the diaphragm seems to be satisfactory provided the zero deflection capacitance is checked occasionally to detect any hysteresis.

In the quest for greater precision in the pressure measurements no fast easy method seems to offer itself with the present experimental arrangement. The necessity for checking the diaphragm calibration a few times in the course of each isotherm involves contact between the gas under investigation and the manometer mercury and may therefore introduce some unreproducibility in the latter. The system of using fixed points for precision manometry has many advantages but is impractical in this application. It is rather remarkable that no very precise method has been developed for measuring pressures in this range, other than the mercury column, which, if pushed to its limit requires tedious attention to many details. An instrument comparable in accuracy and ease of manipulation to the free piston gauge for high pressures would be invaluable in the region around 1 atm.

Apart from the disadvantage of a somewhat lower precision relative to the high pressure expansion method the low pressure method here described has several advantages. The computational work required to obtain values of the second virial coefficient is greatly reduced and no dead space corrections are required. The method may be employed over a fairly wide temperature range. Finally, although in common with all low pressure methods, it is subject to the limitations of mercury-column manometry, this is of less serious concern when gases or vapors with large second virial coefficients are to be measured.

#### ACKNOWLEDGMENT

I am indebted to Dr. W. G. Schneider for his constant encouragement and advice, and to Mr. W. A. Stevenson for his invaluable assistance in the construction of much of the apparatus.

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## NOTES

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### REARRANGEMENT STUDIES WITH C<sup>14</sup>

#### IV. THE ABSENCE OF REARRANGEMENT IN THE SCHMIDT REACTION WITH 3-PHENYLPROPIONIC ACID-2-C<sup>14</sup> \*

C. C. LEE, G. P. SLATER, AND J. W. T. SPINKS

The Schmidt reaction is usually considered to include the transformation of carboxylic acids to amines and of ketones to amides by the action of hydrazoic acid and a strong mineral acid catalyst such as sulphuric acid. The mechanism of the reaction with RCOOH is generally depicted as involving a migration of R, with an unshared electron-pair, to an electron-deficient nitrogen after a union or co-ordination between the carbon atom of the carboxyl and a nitrogen atom of hydrazoic acid (2, 13). No rearrangement in the R group would be expected since the R group migrates with complete retention of configuration as observed in the similar Hofmann, Lossen, and Curtius reactions (2). However, in 1949, Schuerch and Huntress (11) assumed the formation and rearrangement of an intermediate carbonium ion to account for the products obtained in the Schmidt reaction with triethylacetic acid. The degradation of C<sup>14</sup>-labeled carboxylic acids by the Schmidt reaction has been employed in both biochemical (6, 12) and mechanistic (9) studies, and if the degradation of labeled RCOOH should proceed through an intermediate R<sup>+</sup> ion, isotope position rearrangement in the R group would invalidate conclusions drawn from such degradative data.

Recently, Phares and Long (8) have demonstrated the feasibility of degrading C<sup>14</sup>-labeled succinic acid by the Schmidt reaction. However, in this case, it is not possible to tell whether any isotope position rearrangement has taken place in the symmetrical product, ethylenediamine. Phares has also reported the Schmidt degradation of acetic and propionic acids labeled with C<sup>14</sup> in various positions (7). Although the activity in practically all the unlabeled fragments was negligibly low as expected, the degradation of propionic acid-3-C<sup>14</sup> showed an average of 1.5% of the total activity in the C-2 position. Phares attributed this to contamination. On the other hand, if one were to assume that the ethyl cation is an intermediate in the Schmidt reaction with propionic acid-3-C<sup>14</sup>, the activity found in the C-2 position may be conceived as arising from a 1,2-hydride shift in the ethyl cation. Isotope position rearrangement of this order of magnitude in the ethyl cationic system has actually been observed by Roberts and Yancey (10). These workers have found that, in the reaction of ethylamine-1-C<sup>14</sup> with nitrous acid, the resulting labeled ethyl alcohol contained 1.5% of the rearranged product, ethyl-2-C<sup>14</sup> alcohol.

In view of the above considerations, it was thought to be worth while to investigate whether isotope position rearrangement would take place in a Schmidt reaction with an acid which would be expected to give rise to a considerable degree of rearrangement if the reaction were to proceed through a carbonium ion intermediate. The Schmidt reaction with 3-phenylpropionic acid-2-C<sup>14</sup> (hydrocinnamic acid-2-C<sup>14</sup>) was, therefore,

\*For Paper III, see Reference 3.



carried out. Should the reaction proceed through an  $R^+$  intermediate, isotope position rearrangement in the phenylethyl cationic system would be expected since rearrangements of up to 50%, or complete equilibration, of the  $C^{14}$ -labeled atoms from the C-1 to the C-2 positions in the phenylethyl system have been observed in several reactions where the phenylethyl cation was likely involved (3, 4, 5).

3-Phenylpropionic acid-2- $C^{14}$ , or hydrocinnamic acid-2- $C^{14}$ , was prepared from treatment of 2-phenylethyl-1- $C^{14}$ -magnesium chloride with carbon dioxide as previously described (5).

A chloroform solution of 3.5 g. of 3-phenylpropionic acid-2- $C^{14}$  was placed in a three-necked round-bottomed flask fitted with reflux condenser, dropping funnel, thermometer, and magnetic stirrer. An excess of hydrazoic acid in chloroform solution, prepared as described by Wolff (13), was introduced. Concentrated sulphuric acid (12 ml.) was then added dropwise with constant stirring. The reaction vessel was immersed in a water bath maintained at 40–45° C. Additional hydrazoic acid solution was occasionally added to ensure complete reaction. After it had been stirred for 2 hours, the resulting mixture was poured into ice water, and the aqueous layer separated. The organic layer was further extracted with water and the combined aqueous extracts made basic with 50% sodium hydroxide solution. The product was steam distilled into dilute hydrochloric acid. After the distillate had been evaporated to dryness, the residue was recrystallized from absolute ethanol to yield 2.4 g. (65%) of 2-phenylethylamine hydrochloride, m.p. 217° C., lit., m.p. 217° C. (1).

Part of the 2-phenylethylamine hydrochloride was converted to benzoic acid by alkaline potassium permanganate oxidation (4).

All compounds were assayed for radioactivity, the results being listed below.

	3-Phenylpropionic acid-2- $C^{14}$	2-Phenylethylamine hydrochloride	Benzoic acid	
			Run I	Run II
Corrected activity* (c.p.m. on a molar basis)	13,869±93	13,336±84	4±7	7±7

\*All compounds were converted to barium carbonate and counted as infinitely thick samples of constant geometry in a gas flow Geiger counter. Correction for dilution by non-labeled carbon atoms was made by multiplying the observed activity by the number of carbon atoms per molecule in the compound counted.

The fact that the benzoic acid derived from the oxidation of 2-phenylethylamine hydrochloride obtained in the Schmidt reaction with 3-phenylpropionic acid-2- $C^{14}$  contained no radioactivity clearly indicates that there is no isotope position rearrangement. The phenylethyl cation is, therefore, not involved in this reaction. Thus it would appear quite reasonable to conclude that, with the probable exception of such special cases as triethylacetic acid, the Schmidt reaction with  $RCOOH$ , in general, does not involve  $R^+$  ion as an intermediate. One may, therefore, utilize this reaction for degradation of labeled compounds without undue suspicion that isotope position rearrangements might occur during the process of the degradation.

Financial assistance given by the National Research Council of Canada is gratefully acknowledged.

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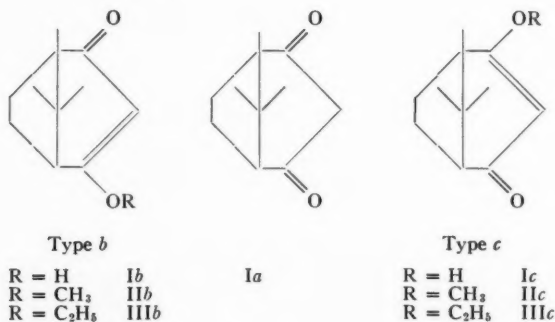
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### DÉRIVÉS DU TRIMÉTHYL-1,8,8 BICYCLO[3,2,1]OCTANE

#### II. SUR LES ÉTHERS CÉTOÉNOLIQUES MÉTHyliQUES ET ÉTHyliQUES DE LA TRIMÉTHYL-1,8,8 BICYCLO[3,2,1]OCTANEDIONE-2,4<sup>1</sup>

H. FAVRE ET B. MARINIER<sup>2</sup>

Nous nous sommes attachés à l'étude des éthers méthyliques et éthyliques de la dicétone I ( $I = Ia \rightleftharpoons Ib \rightleftharpoons Ic$ ) dans le double but d'obtenir des précisions sur l'équilibre dicétonique  $\rightleftharpoons$  cétoénolique de I et d'améliorer la synthèse de l'homoépicamphre que nous avons décrite avec Richer (1).



Les pourcentages respectifs des éthers du type b et du type c dans les divers mélanges obtenus ont été déterminés par l'analyse du pouvoir rotatoire de ces mélanges (1) (voir Tableau I). Nous avons résolu à ces fins le mélange obtenu par le mode opératoire 2 et caractérisé les éthers IIIb et IIIc dont l'un seulement, IIIb, était connu (4). L'éther IIIb, p.f. 72.5°, a été transformé en homoépicamphre, à la manière décrite (1), ce qui établit sans ambiguïté sa structure. Quant à l'éther isomère, p.f. 52°, son pouvoir rotatoire

<sup>1</sup>Cette note est tirée du mémoire de maîtrise de B. Marinier.

<sup>2</sup>Boursier du Conseil National de Recherches du Canada.

TABLEAU I

ACTION DE QUELQUES AGENTS D'ALCOYLATION SUR LA TRIMÉTHYL-1,8,8 BICYCLO[3,2,1]OCTANEDIONE-2,4\*.†

Mode opératoire	Agent d'alcoylation	Ethers obtenus		Composition du mélange, %			
		Rendement, %	$[\alpha]_D$ du mélange	IIb	IIc	IIIb	IIIc
1	CH <sub>3</sub> OH	58.6	-1.4°	55	45		
2	C <sub>2</sub> H <sub>5</sub> N <sub>3</sub>	90	-0.7°			59	41
3	C <sub>2</sub> H <sub>5</sub> OH	78	-10.1°			78	22

\*Le diazométhane conduit avec un rendement quantitatif à un mélange IIb/IIc = 53.9/46.1 (1).

†La méthode d'alcoylation par le formiate d'éthyle (2) n'a pas convenu en raison de la formation prépondérante de produits secondaires (voir pour des produits analogues (2)).

TABLEAU II

DONNÉES CARACTÉRISTIQUES DES ÉTHERS MÉTHyliques IIb et IIc ET DES ÉTHERS ÉTHyliques IIIb et IIIc

Éther	P.f.	$[\alpha]_D^*$	Spectre ultraviolet†		Spectre infrarouge‡	
			$\lambda_{max}$ , mμ	log $\epsilon$	C=O cm. <sup>-1</sup>	$\nu$ C=C cm. <sup>-1</sup>
IIb	56°	-29.7°	250	4.13	1664	1613
IIIb	72.5°	-20.8°	251.5	4.14	1651	1612
IIc	71°	+33.4°	253.5	4.15	1664	1593
IIIc	52°	+27.9°	255	4.17	1660	1588

\* $c = 4.0$ , solution benzéique.

†Éthanol = 95%.

‡Suspension dans le fluorolube.

dextrogyre le rattache bien au type *c*. Nous présentons au Tableau II quelques données caractéristiques des deux éthers éthyliques et pour fins de comparaison, des deux éthers méthyliques partiellement décrits antérieurement (1).

Nous concluons de l'éthérification par le diazométhane principalement que les cétonols Ib et Ic se forment en parties sensiblement égales lorsque la dicétone Ia s'énolise. L'équilibre  $Ia \rightleftharpoons Ib \rightleftharpoons Ic$  se déplace largement en faveur de Ib au cours de l'éthérification lente par l'éthanol; l'empêchement stérique créé par le groupe méthyle en tête de pont est à l'origine de ce fait.

Le mode opératoire 3 convient bien à la synthèse de l'homoépicaembre; il permet d'éviter la séparation laborieuse des éthers IIb et IIc décrite dans le premier travail (1), car par simple cristallisation, on retire 70% d'éther IIIb du mélange brut des éthers IIIb et IIIc.

PARTIE EXPÉRIMENTALE<sup>3</sup>

## Action du diazoéthane sur la dicétone I

A une solution de 3 g. de dicétone I dans 45 ml. d'éther anhydre et 5 ml. d'éthanol 95%, on ajoute rapidement, à 0°, 180 ml. (100% d'excès) d'une solution éthérée de diazoéthane (préparée selon (3, 6), concentration 1.11%). Après un repos de quelques

<sup>3</sup>Les points de fusion (p.f.) ne sont pas corrigés; ils ont été déterminés en tubes capillaires, dans un appareil de Thiele. Les spectres ultraviolets ont été déterminés au moyen d'un spectromètre Beckman DU et les spectres infrarouges, au moyen d'un spectromètre Perkin-Elmer, modèle 112, à simple faisceau et parcours double (optique NaCl). Les pouvoirs rotatoires ont été mesurés en solution benzénique. Les analyses sont de Geller Microanalytical Laboratories, Hackensack, N.J.

minutes, on évapore le solvant sous vide ordinaire et reprend par de l'éther qu'on lave par NaOH 10% et par de l'eau; on sèche et évapore l'éther. Le résidu est distillé; p.é. 150–157° (17 mm.), 3.11 g. (90% de la théorie),  $[\alpha]_D^{25} - 0.7^\circ$  ( $c = 4.37$ ). Ce mélange et ceux résultant de deux préparations similaires (au total 17.3 g.) sont abandonnés à température ambiante pendant quelques jours; on essore alors 8.2 g. de cristaux, p.f. 30–40° s'élevant à 72.5° par cristallisations répétées dans l'éther de pétrole (p.é. 40–60°). Le liquide résiduel est fractionné dans un ballon de Vigreux (à 17 mm., en faisant passer un courant d'azote par le capillaire). Les deux premières fractions laissent déposer l'éthoxy-4 triméthyl-1,8,8 bicyclo[3,2,1]octène-3 one-2 (IIIb) (0.5 g.) qui est recristallisée dans l'éther de pétrole (p.é. 40–60°): prismes incolores, p.f. 72.5°;  $[\alpha]_D^{25} = -20.8^\circ$  ( $c = 4.03$ ). Calculé pour  $C_{13}H_{20}O_2$ : C, 74.96; H, 9.68. Trouvé: C, 75.17; H, 9.68%. La troisième fraction et le résidu de distillation se cristallisent partiellement; l'éthoxy-4 triméthyl-5,8,8 bicyclo[3,2,1]octène-3 one-2 (IIIc) (0.3 g.) est essorée et recristallisée dans l'éther de pétrole (p.é. 40–60°): aiguilles incolores, p.f. 52°;  $[\alpha]_D^{25} = +27.9^\circ$  ( $c = 4.06$ ). Calculé pour  $C_{13}H_{20}O_2$ : C, 74.96; H, 9.68. Trouvé: C, 74.55, 74.32; H, 9.18, 9.58%.

#### *Homoépicamphre*

L'éther IIIb a été transformé, selon la méthode décrite en (1), en homoépicamphre p.f. 202.5°,  $[\alpha]_D^{25} = +133.2^\circ$  ( $c = 4.06$ ), dont la dinitro-2,4 phénylhydrazone fond à 178° seule ou en mélange avec une dinitro-2,4 phénylhydrazone d'homoépicamphre authentique (1).

#### *Action de l'éthanol sur la dicétone I*

Cinq grammes de dicétone I, 10 ml. d'éthanol anhydre et 40 ml. de benzène sont chauffés à l'ébullition à reflux en présence de 50 mg. d'acide *p*-toluènesulfonique; l'eau qui se forme est éliminée au fur et à mesure de sa formation au moyen d'un séparateur d'eau. Après 20 heures, les solvants sont distillés à pression ordinaire, le résidu repris par de l'éther. On isole à la manière habituelle 1.2 g. de dicétone non entrée en réaction et 4.5 g. de neutres (78% de la théorie), solide p.f. brut 55–70°,  $[\alpha]_D^{25} = -10.1^\circ$  ( $c = 4.05$ ). Par cristallisation des parties neutres (éther de pétrole, p.é. 40–50°), on obtient 70% d'éther IIIb pur, p.f. 72.5° (Rupe et Frey (4) indiquent: p.f. 72°).

#### *Action du méthanol sur la dicétone I*

Mode opératoire original de Rupe et Häfliger (5): 5 g. de dicétone I donnent 3.16 g. (58.6% de la théorie) du mélange des éthers IIb et IIc, p.é. 155° sous 22 mm.,  $[\alpha]_D^{25} = -1.4^\circ$  ( $c = 4.01$ ).

#### REMERCIEMENTS

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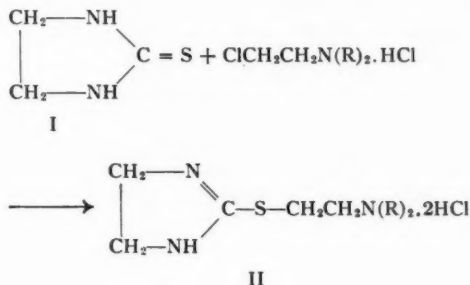
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2-( $\beta$ -DIALKYLAMINOETHYLMERCAPTO)-2-IMIDAZOLINES

STANLEY O. WINTHROP AND GORDON A. GRANT

The reaction (1) of imidazoline-2-thione (I) with alkyl or aralkyl halides readily gives the corresponding 2-alkylmercapto or 2-aralkylmercapto-2-imidazoline salts. This reaction has been used by us for the preparation of a series of 2-( $\beta$ -dialkylaminoethylmercapto)-2-imidazolines (II). 2-Benzhydrylmercapto-2-imidazoline was also prepared by this method.



These compounds were screened by our Pharmacology Department. Some of them were found to have mild analgesic activity.

EXPERIMENTAL<sup>1</sup>*2-( $\beta$ -Dimethylaminoethylmercapto)-2-imidazolinium Chloride Hydrochloride*

Imidazoline-2-thione<sup>2</sup> (10 g., 0.093 mole) and  $\beta$ -dimethylaminoethylchloride hydrochloride (13.4 g., 0.093 mole) were dissolved in 175 ml. of isopropanol and refluxed for 48 hours. The solution was then evaporated to about 75 ml. On cooling, 12 g. of product separated out, m.p. 179–183° C. Two recrystallizations from isopropanol raised the melting point to 183.5–184.5° C. Calc. for  $\text{C}_7\text{H}_{17}\text{N}_3\text{SCl}_2$ : C, 34.15; H, 6.96; S, 13.02; Cl, 28.80. Found: C, 34.22; H, 7.02; S, 13.02; Cl, 28.89.

*2-( $\beta$ -Diethylaminoethylmercapto)-2-imidazolinium Chloride Hydrochloride*

In the same manner as the above procedure, imidazoline-2-thione (7.8 g., 0.075 mole) and  $\beta$ -diisopropylaminoethylchloride hydrochloride (15.1 g., 0.075 mole) gave 20 g. of product, m.p. 217–219° C. One recrystallization from ether–ethanol raised the melting point to 218–219° C. Calc. for  $\text{C}_{11}\text{H}_{26}\text{N}_3\text{SCl}_2$ : N, 13.91; S, 10.60; Cl, 23.47. Found: N, 15.05; S, 11.96; Cl, 25.82.

*2-( $\beta$ -Diisopropylaminoethylmercapto)-2-imidazolinium Chloride Hydrochloride*

This compound, m.p. 188–190° C., was prepared in a 92% yield by the same procedure as were the previous two homologues. One recrystallization from ethanol gave an analytically pure material, m.p. 193–194° C. Calc. for  $\text{C}_9\text{H}_{21}\text{N}_3\text{SCl}_2$ : N, 15.32; S, 11.69; Cl 25.86. Found: N, 15.05; S, 11.96; Cl, 25.82.

<sup>1</sup>All melting points are uncorrected.

<sup>2</sup>Sharples Chemical Inc., Philadelphia 9, Pa.

*2-(β-Diisopropylaminoethylmercapto)-2-imidazoline (Free Base)*

2-(β-Diisopropylaminoethylmercapto)-2-imidazolinium chloride hydrochloride (12.5 g., 0.0415 mole) was dissolved in a 100 ml. of methanol and a solution of sodium methoxide (4.55 g., 0.083 mole) in 100 ml. of methanol was slowly added with stirring. The solution was then filtered to remove the precipitated sodium chloride and the filtrate evaporated down *in vacuo* at room temperature, leaving 7 g. of product as a viscous oil. Attempts to induce this oil to crystallize have not been successful to-date. The free base decomposed readily on heating with the production of a mercaptan-like odor. It was characterized by conversion to its acid salts.

Free base (1.0 g.) was dissolved in 10 ml. of ether and excess hydrobromic acid in a little isopropanol was added. The 2-(β-diisopropylaminoethylmercapto)-2-imidazolinium bromide hydrobromide precipitated as an oil which crystallized on trituration with an ether-isopropanol mix to yield 1.3 g. with m.p. 202–205° C. One recrystallization from ether-ethanol raised the melting point to 206–207° C. Calc. for  $C_{14}H_{25}N_3SBr_2$ : N, 10.74; S, 8.19; Br, 40.85. Found: N, 10.72; S, 8.37; Br, 40.92.

The free base was also converted to its dihydrogen sulphate addition salt by an identical procedure. The salt melted at 145–146° after two recrystallizations from ether-isopropanol. Calc. for  $C_{11}H_{27}N_3S_2O_8$ :  $SO_4$  ion, 15.04; N, 9.87. Found:  $SO_4$  ion, 15.03; N, 9.73.

*2-Benzhydrylmercapto-2-imidazolinium Bromide Hydrobromide*

Imidazoline-2-thione (2.55 g., 0.025 mole) and benzhydrylbromide (6.2 g., 0.025 mole) were dissolved in 20 ml. of ethanol and refluxed for 2 hours. The ethanol was then removed *in vacuo* and the oil residue crystallized from an isopropanol-benzene mix to yield 6.2 g. of product, m.p. 135–150° C. Two recrystallizations from ether-isopropanol raised the melting point to 174–176° C. Calc. for  $C_{16}H_{17}N_2SBr_2$ : C, 55.02; H, 4.91; N, 8.02; Br, 22.89. Found: C, 55.10; H, 5.04; N, 8.00; Br, 22.78.

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